Book I of The History examines the historical episodes leading up to the Peloponnesian War. After presenting some background information on the history of the region, Thucydides asserts his belief that the true cause of the war was, "The growth of the power of Athens and the alarm which this inspired in Lacedaemon. . ." (24). But Thucydides also insists that this cause tends to be shrouded by the rhetoric of the combatants, who maintain that other factors brought about the war.

The first key episode examined by Thucydides is the affair of Epidamnus. A city founded by colonists of Corcyra, which in turn was a colony of the city-state of Corinth, Epidamnus found itself the victim of barbarian invasions. The people of Epidamnus appealed to Corcyra for assistance, and after receiving none, took their pleas to Corinth which answered the call by dispatching troops and settlers to the city. Corcyra responded to Corinth’s action by sending their own fleets to the city. The eventual result was a naval war between Corinth and Corcyra, with Corcyra, superior in terms of naval strength, winning a decisive victory.

Corinth would spend the following year augmenting its navy in order to exact revenge from Corcyra. Both city-states petition Athens for assistance. To woo the Athenians, the Corcyraeans argue that alliance with Corcyra would be an important step for Athens given the likelihood of war in the near-future with jealous Sparta. Besides helping Corcyra to counter the injustices committed against it by its mother colony, an alliance would be in Athens’ own interest, argue the Corcyraeans, due to the power of Corcyra’s navy, as well as the strategic location of Corcyra within the passage between Italy/Sicily and Athens. Corinth counters by asserting that it possesses the right to punish its own dependencies, including Corcyra. Moreover, the Corinthians claim that for Athens to pursue a great naval alliance with Corcyra would be tantamount to chasing short-term gain at the price of long-term instability.

In the end, Corcyra’s arguments carry the day, and Athens dispatches 10 ships to aid Corcyra. Corinth initiates its campaign against Corcyra, as planned, and sails on Corcyra with a large fleet. Corinth and its allies fight an epic naval battle against the Athenian/Corcyraean alliance near Corcyra. The battle has an ambiguous result; while the Corinthian fleet does more damage than the Corcyraeans, it also flees the area upon encountering Athenian forces.

Thucydides proceeds to discuss the second key event leading up to the Peloponnesian war: the affair of Potidæa. A Corinthian colony that is also a tributary ally of Athens, Potidæa finds itself caught in the middle of the Athens-Corinth conflict. Potidæa decides to revolt against Athens after receiving assurance from Sparta that Sparta would invade Athens if Athens should take measures against Potidæa. While Potidæa was deciding to revolt, Athens had already dispatched a fleet of thirty ships and 1000 heavy infantry to the city with orders to take the Potidæans captive. Angered at the invasion of her colony by Athens, Corinth calls a conference of her allies at Sparta. Corinth attempts to spur Sparta to take action against Athens, arguing that Sparta's conservative, plodding strategy has allowed the Athenians to gain too much strength. Several Athenian citizens respond to Corinth’s efforts to incite Sparta by reminding the Greeks of the paramount role Athens played in the recent Median war against the barbarians. They also appeal to the principle of "might makes right" in justifying Athens’ recent military adventures. The Spartan king Archidamus follows the Athenians and suggests that the Spartans take the prudent course of delaying action until they have at least sufficient monetary resources to engage wealthy Athens. The king’s advice is ignored, however, as the Spartan assembly decides effectively to declare war against Athens (so long as Sparta's allies consent).