This study aims to identify the hydrogeochemical processes influencing the high fluoride concentrations in groundwater of the Nairobi area, Kenya. For this purpose 16 groundwater samples were collected and analysed. Fluoride concentrations above the WHO standard are found in the downstream areas. The high F- concentrations are correlated with high sodium and pH and low Ca2+ concentrations. Weathering of sodium-rich alkaline igneous rocks causes a pH increase resulting in an increase in HCO3- and CO32- by dissolution of CO2. Groundwater becomes oversaturated compared to calcite and calcite precipitation occurs, leading to a decrease in Ca2+. This causes a sub-saturation with respect to fluorite and dissolution of fluorite increases the F- concentration. These reactions were modelled using the PHREEQC model and the results showed a good agreement with the measured groundwater quality, indicating that the proposed reactions are plausible for explaining the observed concentrations in groundwater.