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Hydrogeochemistry of shallow and deep aquifer groundwaters collected from boreholes and wells (N=47) along the flow lines of western margins of Kumamoto basin, has been studied in order to evaluate the geochemical controls on fluoride concentrations. Kumamoto city, situated at the central part of Kyushu island in southern Japan, is considered as the largest urban groundwater city in Japan. 100% people of this city depends on groundwater for their drinking purpose. Groundwater aquifers are composed of Quaternary volcanic (pyroclastic) flow deposits. In both shallow and deep aquifers, groundwaters evolve along the down flow gradient from oxidizing conditions of recharge area to the reducing conditions of stagnant area of Kumamoto plain.

Groundwater pH is near-neutral to alkaline (7.05-9.45) while sodium and bi-carbonate is the predominant cation and anion respectively. Groundwaters are mainly Na-HCO₃ type along with few Na-Cl type samples. F⁻ concentration ranges between 0.1 to 1.57 mg/L with an average of 0.7 mg/L whereas 47% shallow groundwater and 21% deep groundwater exceeded the Japanese drinking water standard (0.8 mg/L). With respect to groundwater chemistry, high F⁻ concentrations were mainly observed in Na-HCO₃ type groundwater and low concentrations in Ca-HCO₃ type groundwater. F⁻ is positively correlated with HCO₃⁻ and Na⁺, indicating that groundwater with high HCO₃⁻ and Na⁺ contents help in dissolving of some fluoride-rich minerals. Groundwaters with higher F⁻ contents have relatively higher pH value, suggesting that alkaline environment favors the replacement of exchangeable F⁻ in fluoride-rich minerals by OH⁻ in groundwater. Different ionic relationships imply that the geochemical behavior of fluoride in groundwater is also influenced by the ion-exchange process which release Na⁺ to the groundwater and removes Ca²⁺ ions from groundwater. Thermodynamic relationship between the activities of Ca²⁺ and F⁻ indicate that groundwater is undersaturated with respect to fluorite (CaF₂). However upper limit of fluoride (F⁻) is controlled by the precipitation of Ca²⁺ ion. These observations reflect that fluoride concentration in Kumamoto groundwater is mainly controlled by the dissolution and precipitation processes of fluoride and Ca-rich minerals.

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