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Occurrence and mobility of major and trace elements in groundwater from pristine volcanic aquifers in Jeju Island, Korea

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ABSTRACT

Major and trace elements in groundwater from basaltic aquifers in pristine conditions were investigated in a volcanic island to evaluate sources, sinks, and mobility of elements over a wide range of mineralization conditions with total dissolved solids from 50 mg/L to 3400 mg/L. Groundwater was highly undersaturated with respect to primary silicate minerals, indicating that dissolution of basaltic rocks may continue under conditions with precipitation of calcite and secondary silicates. Evolution of B/Cl ratio in groundwater from marine aerosols to basaltic rocks showed that the ratio could be used as a conservative tracer for interactions between water and basaltic rocks. Relative mobility (RM) of elements calculated using the concentrations of elements in the local basaltic rocks and those in groundwater showed that mobility decreased in the order of B > Rb > Na > K > Mg > Ca > Mo > V > Si > Sr > Sc > P > U > Zn > Pb > Cr > Cu > Ba > Ni > Ti > (Mn, Al, Fe, Co, Th) indicating that oxyanion-forming elements and alkali metals had the highest mobility. Compared to average RM, V had decreased mobility, and Fe and Mn had increased mobility in anoxic groundwater while V, Mo, and U had higher mobility in oxic-alkaline water. The sources of V, Cr, Cu, and Zn in rocks were estimated using the partition coefficients between minerals and basaltic melt, and the disparity between sources and mobility indicated that sinks are more important for controlling the concentrations of these elements in groundwater than the contents in the rocks. Principal component analysis (PCA) of hydrogeochemical parameters in groundwater produced three principal components (PC) which represent dissolution of basaltic rocks without significant attenuation of released solutes, higher degree of water–rock interactions resulting in oxic-alkaline conditions, and attenuation of Zn and Cu in higher pH, respectively. Spatial distribution of PCs revealed that groundwater with elevated concentrations of mobile elements was concentrated in the southwestern area and that concentrations of V and Cr were more scattered, which is likely to be controlled by pH and redox states of groundwater as well as degree of water–rock interactions.

1. Introduction

Basaltic rocks have a considerable number of solid phases with high dissolution rates, including olivine, glass, and pyroxenes. Both field and laboratory studies have shown that the chemical composition of surface and groundwater can be significantly affected by basaltic rocks, due to their high reactivity during water–rock interactions (Meybeck, 1987; Bluth and Kump, 1994). The hydrogeochemistry of natural water in basaltic rocks has been widely investigated in terms of the chemical weathering and mobility of elements (Louvat and Allegre, 1997; Stefansson and Gislason, 2001). The chemical composition of natural water in Iceland was studied in terms of the thermodynamic equilibrium between primary silicate minerals and water (Gislason and Arnorsson, 1993; Stefansson et al., 2001), and the rate of chemical weathering in basaltic terrains (Gislason and Eugster, 1987; Stefansson and Gislason, 2001). Pokrovsky et al. (2005) determined the rate of chemical weathering of basalts and element mobility by combining a chemical and mineralogical analysis of solids and the chemistry of natural water in Central Siberia.

For the active volcanic area of Mt. Etna in Italy, studies involving the sources of solutes, water quality, mobility, and thermodynamic

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modeling were conducted around the volcano where groundwater is affected by inputs of CO_2-rich magmatic gas and changes in the volcanic plumbing system (Giammanco et al., 1998; Aiuppa et al., 2000a, 2003). The groundwater quality of volcanic aquifers is important because the dissolution of aquifer materials can provide elevated levels of dissolved constituents. Some studies of major and minor elements in groundwater have been conducted to determine chemical weathering and groundwater quality (Edmunds et al., 2002; Van Der Weijden and Pacheco, 2003). However, the behavior of dissolved trace elements in groundwater in volcanic areas where the volcano is inactive has not been investigated extensively.

In this study, the behavior of major and trace elements in pristine groundwater from Quaternary basaltic rocks with various levels of water–rock interactions is investigated on a volcanic island with negligible historic signature of volcanic and geothermal activity. The aims of this study are: 1) to characterize the variation of the dissolved concentrations of major and trace elements due to water–rock interactions, 2) to evaluate their geochemical mobility and determine the possible sources and sinks of the elements in groundwater, and 3) to provide baseline groundwater quality of volcanic aquifers which are the sole source of drinking water on the island where significant land use changes are expected due to higher development pressure.

2. Study area

2.1. Geologic and hydrogeologic setting

The study area is a 589 km^2 mountainous region (200–600 m a.s.l.) of Jeju Island, Korea, corresponding to 32% of total surface area of the island (Fig. 1). The island was formed by Quaternary basaltic and trachytic volcanism from 1.2 Ma to 0.025 Ma. The island has no active volcanoes at present (Park and Kwon, 1993a). The basaltic rocks consist of numerous lava flows and cover most of the surface area of the island, which are highly permeable and form the principal aquifers (Koh et al., 2005a). The basaltic rocks are underlain by the Seogwipo Formation which consists of consolidated or semi-consolidated hydrovolcanic tuffs (Sohn et al., 2002). The basement rock on the island consists of pyroclastic rocks, welded tuff, lapilli tuff, and granite (Koh et al., 2005a). In the eastern part of Jeju, basaltic rocks are found at sea level whereas the Seogwipo Formation is present near sea level in other areas that have upward slopes toward the center of the island (Won et al., 2006).

The land use of the study area is mainly natural cover and pasture. Groundwater of the area is much less affected by anthropogenic activities and the direct effect of seawater intrusion is not observed (Koh et al., 2009). Park et al. (2014) showed that 69% of the total recharge occurred in the elevation over 200 m using a distributed water balance model, which indicates the mountainous region would be a critical groundwater recharge zone. The land use of the island has undergone dramatic changes in the coastal area (<200 m a.s.l.) and proportion of anthropogenic land uses increased from 41% in 1980 to 73% in 2000. The anthropogenic land uses of agricultural and recreational areas also affected the mountainous region and their proportion increased from 3% in 1980 to 21% in 2000 though much of them are concentrated near the boundary of the coastal and mountainous region (Ha et al., 2009). Considering this temporal trend in land use patterns, groundwater quality in the mountainous region may be adversely affected by the change in the near future.

2.2. Mineralogic and chemical composition of basaltic rocks

Park et al. (1999) compiled data regarding the concentrations of the major elements in the whole rocks of Jeju Island, and showed that the majority of basaltic rocks correspond to basalt and trachybasalt. Based on the classification of alkalic and sub-alkalic basalts, it was confirmed that alkali basalts are predominant and tholeiitic basalts are only found in coastal areas. The results of a modal analysis of the basaltic rocks showed that plagioclase (An_{45-65}) is the most abundant mineral comprising 60 vol. % (Won, 1976). The average volume percentage of the groundmass with crystal sizes smaller than 0.1 mm is 85% and for phenocrysts (plagioclase, olivine, clinopyroxenes, and titanomagnetite) the values are 10.7, 2.4, 1.4, and 0.2%, respectively. The groundmass includes lath-type

Fig. 1. Location map of groundwater sampling sites. Location of a borehole where rock samples for chemical analysis of B and Cl were taken are shown as “X” mark in the southwestern part of the study area.