Quartz control of high germanium/silicon ratios in geothermal waters

Matthew J. Evans
Louis A. Derry   Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York 14853, USA

ABSTRACT

Germanium/silicon (Ge/Si) ratios in Himalayan hot-spring fluids show a wide range, 4–1000 μmol/mol. Equilibrium calculations with an ideal solid-solution model of germanium in quartz yield Ge/Si_fluid ratios consistent with data from high-temperature reservoirs but do not fit lower temperature observations, in part because of kinetic constraints. A model of progressive Si loss via precipitation of Ge-poor quartz (Rayleigh distillation) can produce the extreme Ge/Si_fluid ratios observed in the Himalayan and other systems. Small variations in Si loss, mixing with surface waters, and/or disequilibrium can produce the observed variability in Ge/Si_fluid within a given hydrothermal system. The high level of Si loss (~95%) required to reach extreme Ge/Si_fluid ratios is consistent with reaction-path calculations for the evolution of a geothermal fluid from its reservoir to surface temperatures and implies that Ge/Si ratios can be a useful tracer of silica dynamics in hydrothermal systems.

Keywords: germanium, hot springs, water-rock interaction, silicon, quartz.

INTRODUCTION

Germanium's behavior is similar to that of silicon in most geologic environments, and germanium/silicon (Ge/Si) ratios have been used as a tracer of silica behavior and sources in surface environments (Murnane and Stallard, 1990; Froelich et al., 1992; Kurtz et al., 2002). In streams, Ge/Si ratios (typically <1 μmol/mol) are depleted relative to bedrock, which has Ge/Si = 1.5–3.0 μmol/mol (Mortlock and Froelich, 1987). In contrast, Ge/Si ratios in thermal waters from both mafic and felsic terranes are often very high, from 2 to 1000 μmol/mol. Arnorsson (1984) examined hot springs and well waters from the geothermal system of Iceland and reported Ge/Si_fluid ratios from 3 to 185 μmol/mol, and Criaud and Fouillac (1986) reported ratios ranging from 2 to 1000 μmol/mol in springs from the Massif Central in France. High-temperature seafloor hydrothermal fluids have Ge/Si_fluid ratios between 3 and 20 μmol/mol, whereas low-temperature submarine fluids show more variability (0.9–45 μmol/mol) (Mortlock et al., 1993). The large disparity between Ge/Si ratios of thermal waters and surface waters makes Ge/Si a potentially useful tracer of hot-spring input, and the variability may provide clues to mineral-alteration or mineral-precipitation processes in hydrothermal systems (Mortlock et al., 1993). Although Ge enrichment over Si in thermal waters is well documented, no detailed explanation of the enrichment process or of the wide variability of Ge enrichment is yet available. We present (1) data from Himalayan hot springs that show a wide range of Ge/Si ratios and (2) modeling results that show that quartz solubility and Ge substitution into the quartz mineral lattice both play important roles in determining Ge behavior in thermal waters.

SAMPLES AND METHODS

In central Nepal, numerous geothermal springs are found near the Main Central thrust and in the north-trending Mustang graben (Galy and France-Lanord, 1999; Grabczak and Kotarba, 1985). The springs generally flow from the metapelites, gneisses, quartzites, and schists of the High Himalayan Crystalline Series and Lesser Himalayan Sequence. Advection of these deep-seated crustal rocks, high internal heat production, and rapid erosion of the thrust wedge result in steep thermal gradients in the crystalline rocks of the Himalayan front (Royden, 1993). Meteoric water circulation within these rocks produces hydrothermal activity in the deeply incised valleys of the Kali Gandaki, Mayongdi, Modi, Seti, Marsyandi, Bhuri, Chilime, Langtang, and Bhote Kosi Rivers. Temperatures in the Himalayan thermal waters range from 20 to 70 °C. Total dissolved solids (TDS) values range from 200 mg/L to 14 000 mg/L and average 3000 mg/L. Samples were taken over several field seasons and include 49 samples from 22 thermal spring locations.

Water samples were filtered and acidified in the field and stored in acid-washed bottles. Ge concentrations were determined by isotope-dilution hydride generation (Mortlock and Froelich, 1996) on a Finnigan Element II inductively coupled plasma–mass spectrometer (ICP-MS) at Cornell University. Reproducibility on multiple runs of the same sample with varying dilutions and spike amounts (enriched [70]Ge tracer) is better than 3%, and reagent blanks are ~0.5 ppt Ge. Si concentrations in waters were determined by molybdate blue spectrophotometry. Mineral samples were powdered, fused, and then dissolved in nitric acid. Dilutions were made immediately to avoid precipitation from the metastable Si-rich solution. Si concentrations were determined by ICP-MS for quartz and ICP–atomic-emission spectrometry for other minerals. Ge concentrations were determined by using the procedure already described.

GEOCHEMICAL RESULTS

Himalayan springs have high [Ge], to 684 nM, and Ge/Si_fluid ratios range from 4 to >1000 μmol/mol[1]. The thermal waters are saturated to supersaturated with quartz; [Si] ranges from 160 to 2700 μmol. In most cases, Ge/Si_fluid ratios range from 50 to 150 μmol/mol. [Ge] and [Si] are not correlated with temperature, and the highest Ge/Si_fluid ratios are found in the springs with intermediate temperatures (45–55 °C), similar to the springs in the Massif Central (Criaud and Fouillac, 1986) and Iceland (Arnorsson, 1984).

In addition to thermal waters, we analyzed hydrothermal vein quartz samples for Ge and Si concentrations (Table 1). All the sampled veins crosscut the local metamorphic fabric and fluid-inclusion homogenization temperatures indicate formation temperatures of ~250–300 °C for the veins (R. Darling, 2002, personal commun.). [Ge] in the quartz ranges from 0.4 to 2.3 ppm, resulting in Ge/Si_quartz ratios from 0.3 to 1.8 (mean = 1.2 μmol/mol). These ratios are similar to quartz from Icelandic fossil geothermal systems ([Ge] = 0.1–1.3 ppm and Ge/Si_quartz = 0.1–1) (Arnorsson, 1984). Bernstein (1985) reported [Ge] in quartz ranging from 0.8 to as high as 8.0 ppm, resulting in Ge/Si_quartz ratios from 0.66 to 6.5 μmol/mol, respectively. The gneisses that host most of the central Nepal springs have a Ge/Si ratio of 2.0–2.5 μmol/mol. Ge concentrations were determined for mineral separates from these gneisses; Ge/Si ratios for biotite are ~4 μmol/mol,

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[1]GSA Data Repository item 2002120, Table DR-1, Temperatures, Ge and Si concentrations, Ge/Si ratios, and sample locations for central Nepal hot springs, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

TABLE 1. MINERAL Ge CONCENTRATIONS AND Ge/Si RATIOS

Sample	[Ge] (ppm)	Ge/Si (µmol/mol)
Quartz (MLB 34)	1.10	0.89
Quartz (MLB 74)	0.44	0.35
Quartz (MLB 80)	0.92	0.74
Quartz (MLB 89)	1.01	0.84
Quartz (GA 75)	2.22	1.74
Quartz (GA 209)	1.53	1.20
Plagioclase	1.87	1.83
Muscovite	1.50	2.37
Biotite	2.52	4.04
Kyanite	0.78	1.73

Note: Samples were from crosscutting hydrothermal vein quartz from central Nepal and mineral separates from host gneiss. Quartz veins were sampled in Bhuri Gandaki (GA 209), Trisuli (MLB 34), Mayongdi (MLB 74), Kali Gandaki (MLB 80), and Modi Khola (MLB 89) river valleys as well as the Lari mine at 4 km elevation between Bhuri Gandaki and Trisuli valleys (GA 75). Mineral separates were collected from High Himalayan Crystalline Series gneisses near Dordi Khola.

Figure 1. Log K values for hydrolysis of $GeO_{2(hex)}$ and SiO_2, and Ge/Si_{fluid} (µmol/mol) of fluid in equilibrium with Ge-bearing quartz (1.2 ppm Ge) as function of temperature. Experimental data (filled circles) for $GeO_{2(hex)}$ solubility are from Pokrovski and Schott (1998).

whereas the ratios for plagioclase, muscovite, and kyanite are ~2 µmol/mol (Table 1).

MODEL RESULTS AND DISCUSSION

Two mechanisms have been proposed to explain the high Ge/Si_{fluid} ratios in thermal waters. The first is a thermodynamically driven, temperature-dependent equilibrium between Ge-bearing silicate minerals and a fluid. The second is a fluid-mineral fractionation caused by progressive precipitation of Ge-poor secondary minerals as the fluid cools and/or mixes with surface waters, producing a Ge-enriched fluid phase. By using an equilibrium model, Pokrovski and Schott (1998) found that the Ge/Si ratio for a fluid in equilibrium with Ge-wollastonite $[Ca(Ge_xSi_{1-x})O_3]$ increased by an order of magnitude as temperature rose from 25 to 500 °C. In their work on Pacific Ocean hydrothermal vents and plumes, Mortlock et al. (1993) showed that the highest Ge/Si_{fluid} ratios were found in the lower temperature vent fluids and that high-temperature vents show a trend of increasing Ge/Si ratios with decreasing Si concentration. Similar to Arnorsson (1984), Mortlock et al. (1993) suggested that this Ge enrichment in the fluid is caused by formation of secondary silicate minerals with low Ge/Si ratios.

It is widely accepted that silica behavior in hydrothermal systems is predominantly controlled by quartz solubility (Holland and Malinin, 1979; Fournier, 1985; Rimstidt, 1997). The Himalayan hydrothermal fluids are all at or above quartz saturation, and quartz is by far the most abundant silicate mineral observed in hydrothermal veins in central Nepal. These observations suggest that quartz solubility is the primary control on Ge in the hot-spring fluids, and we therefore evaluate both models described as they apply to quartz precipitation. First we apply an equilibrium model using thermodynamic properties of $GeO_{2(hex)}$, SiO_2, $Si(OH)_4$, and $Ge(OH)_4$ to calculate the Ge/Si ratio of a fluid in equilibrium with a Ge-bearing quartz. Second, we calculate the Ge/Si ratio of a thermal water by using a Rayleigh (batch) model of incremental quartz precipitation.

EQUILIBRIUM MODEL

For the equilibrium calculation we make the assumption that an ideal solid solution exists between quartz and the Ge analogue to quartz (GeO_2). An ideal solid solution between the Si and Ge end members has been shown to exist in synthetic talc (Martin et al., 1996), as well as in glasses and crystals of sodium feldspar composition (Capobianco and Navrotsky, 1982). Germanium dioxide exists as two crystalline phases: the hexagonal form with tetrahedral coordination similar to alpha quartz $[GeO_{2(hex)}]$ and the tetragonal form with octahedral co-ordination similar to rutile $[GeO_{2(tet)}]$ (Smith and Isaacs, 1964; O'Neill, 1986; Balitsky et al., 1997). Although the hexagonal form is more stable at high temperatures (>1000 °C), both exist as metastable phases
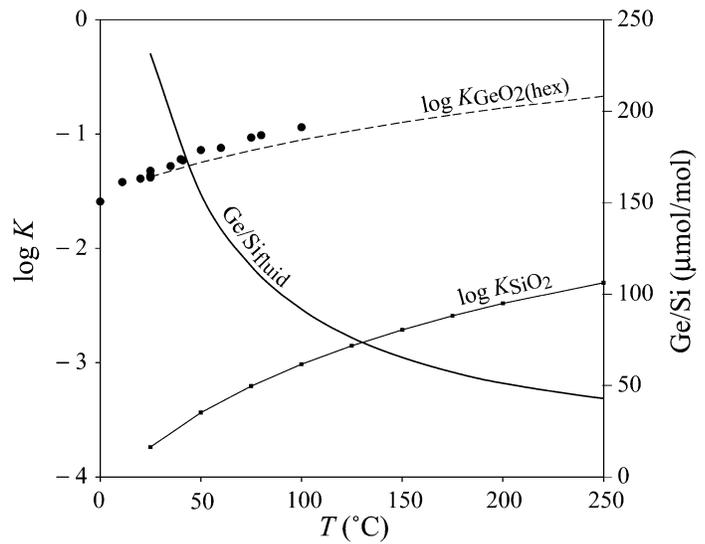
at room temperature, and we have chosen $GeO_{2(hex)}$ for its similarity to quartz at the temperature range of interest. The calculation is performed by using published thermodynamic parameters for the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Tanger and Helgeson, 1988) and the following four equations. The hydrolysis equations for the end members of the Ge-Si solid solution are

$$GeO_{2(hex)} + 2H_2O = Ge(OH)_4 \quad \text{and} \tag{1}$$

$$SiO_2 + 2H_2O = Si(OH)_4. \tag{2}$$
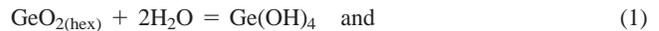
By combining these equations, one can determine the equilibrium Ge/Si_{fluid} ratio with the following:

$$\frac{Ge}{Si_{fluid}} = \frac{a_{Ge(OH)_4}}{a_{Si(OH)_4}} = \frac{K_{GeO_{2(hex)}}}{K_{SiO_2}} \times \frac{a_{GeO_{2(hex)}}}{a_{SiO_2}}, \tag{3}$$

where $a_{GeO_{2(hex)}}$, a_{SiO_2}, $a_{Si(OH)_4}$, and $a_{Ge(OH)_4}$ are the activities of $GeO_{2(hex)}$, SiO_2, silicic acid $[Si(OH)_4]$ and germanic acid $[Ge(OH)_4]$, respectively, and $K_{GeO_{2(hex)}}$ and K_{SiO_2} are the equilibrium constants for the hydrolysis of $GeO_{2(hex)}$ and SiO_2. Values for $K_{GeO_{2(hex)}}$ and K_{SiO_2} were calculated from 25 to 250 °C along the saturation curve of water by using revised HKF parameters for water and quartz from SUPCRT92 (Johnson et al., 1992), for $GeO_{2(hex)}$ and $Ge(OH)_4$ from Pokrovski and Schott (1998), and for $Si(OH)_4$ from Stefansson (2001). For ideal solid solution between quartz and germanium dioxide $(Si_{(1-x)}Ge_x)O_2$,

$$a_{GeO_{2(hex)}} = x \quad \text{and} \tag{4}$$

$$a_{SiO_2} = (1 - x). \tag{5}$$

For our purposes, we used the average [Ge] of the Himalayan quartz veins (1.2 ppm), which results in a quartz with a Ge/Si ratio of 1 µmol/mol and a value for $x = 1 \times 10^{-6}$.

Figure 1 shows the calculated Ge/Si_{fluid} in equilibrium with a Ge-bearing quartz and the log K values of the hydrolysis reactions for both $GeO_{2(hex)}$ and SiO_2. The resultant Ge/Si ratio in the equilibrium fluid decreases with increasing temperature (Fig. 1) from 230 µmol/mol at 25 °C to 43 µmol/mol at 250 °C. This result contrasts with the wol-
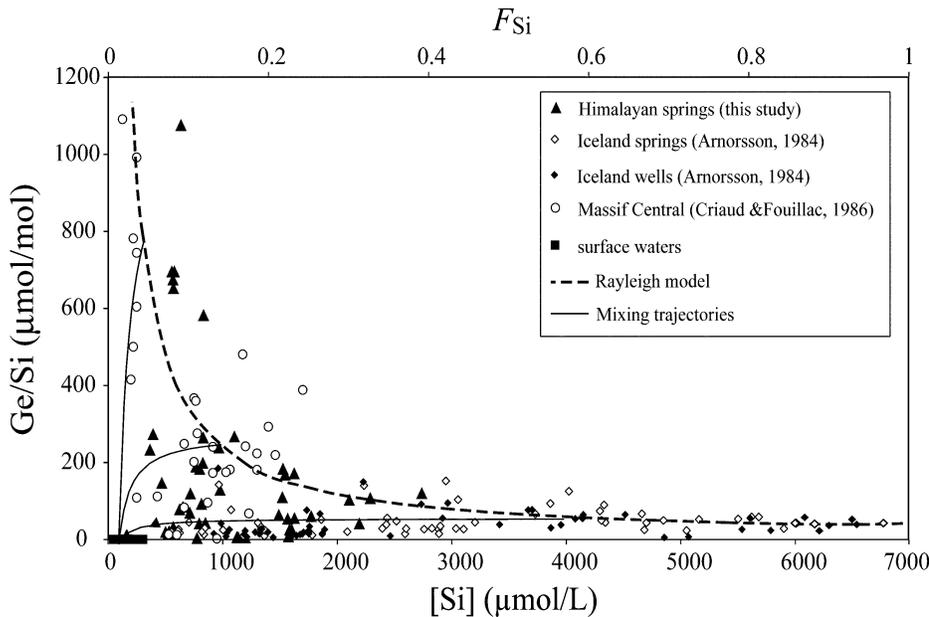
Figure 2. Rayleigh model results plotted with measured Ge/Si ratios (μmol/mol) and Si concentrations from various thermal springs. Initial Ge/Si ratio of 40 and temperature-dependent α are based on results of equilibrium model. Initial [Si] of 7000 μmol/kg for Rayleigh model is based on quartz solubility (Rimstidt, 1997) at initial temperature of 250 °C. [Si] values for some Iceland wells continue to ~9000 μmol/kg with average Ge/Si$_{fluid}$ = 32 (Arnorsson, 1984). Solid curves illustrate example trajectories of hydrothermal fluid mixing with average surface waters. Mixing with surface waters at various stages of hydrothermal fluid evolution will produce family of mixing curves that will appear to radiate from surface-water values.

lastonite calculation performed by Pokrovski and Schott (1998) in which the Ge/Si$_{fluid}$ increased with temperature. The high-temperature results of the equilibrium model are consistent with data from Iceland wells, which have average Ge/Si$_{fluid}$ = 42 at 235 °C (Arnorsson, 1984). The maximum Ge/Si$_{fluid}$ of 230 μmol/mol at 25 °C is well below the highest observed ratios from the Massif Central and central Nepal, and it is unlikely that fluids are in equilibrium with quartz at such low temperatures. Furthermore, the equilibrium model predicts that Ge/Si$_{fluid}$ should be well correlated with temperature, at odds with our data. These observations suggest that the equilibrium model cannot produce the observed high Ge/Si$_{fluid}$ ratios, but has a strong influence on Ge/Si behavior at geothermal reservoir temperatures.

RAYLEIGH DISTILLATION

Thermal waters cool as they rise to the surface either by simple conductive cooling or by mixing with surface waters, and quartz is precipitated from these fluids. We have used a Rayleigh distillation model to examine the evolution of the Ge/Si ratio of a fluid as it cools and Si is removed from solution by quartz precipitation.

In a system progressively precipitating quartz, the Ge/Si ratio of the fluid is a function of the initial fluid ratio and the fraction of Si that has been removed by precipitation:

$$(Ge/Si_{fluid}) = Ge/Si_0 \times F_{Si}^{(\alpha-1)}, \qquad (6)$$

where F_{Si} is the remaining fraction of the initial solution [Si], (Ge/Si$_{fluid}$) is the ratio in the fluid as a function of F_{Si}, Ge/Si$_0$ is the initial ratio (at F_{Si}=1), and α is the fractionation factor defined as the instantaneous quartz ratio divided by the instantaneous fluid ratio:

$$\alpha = (Ge/Si_{quartz})/(Ge/Si_{fluid}). \qquad (7)$$

The instantaneous Ge/Si$_{quartz}$ is then

$$(Ge/Si_{quartz}) = \alpha \times (Ge/Si_{fluid}). \qquad (8)$$

On the basis of the equilibrium model and in agreement with high-temperature data from Icelandic geothermal wells (Arnorsson, 1984), (Ge/Si)$_0$ = 40. We used the results from the equilibrium model to find a temperature-dependent fractionation factor between quartz and the equilibrium fluid. This α ranges from an initial value of 0.023 at F_{Si} = 1 to 0.0054 at F_{Si} = 0.03. We note that the resultant Ge/Si$_{fluid}$ ratio is not very sensitive to the choice of α, but the fractionation factor does strongly affect the Ge/Si ratio of the precipitated quartz, particularly at lower values of F_{Si}. By using our α values, we obtain Ge/Si$_{quartz}$ ratios from 1 to 6, within the reported range (Bernstein, 1985).

The results of the Rayleigh model are consistent with data from a variety of systems and settings (Fig. 2). For a reservoir temperature of ~250 °C (consistent with the quartz fluid-inclusion data), the solid-solution model yields a Ge/Si$_0$ ratio of 43, which corresponds to a quartz equilibrium [Si] of ~7000 μmol (Rimstidt, 1997). High Ge/Si$_{fluid}$ ratios are produced at lower [Si] (low F_{Si}). The extreme Ge/Si$_{fluid}$ ratios (400–1000 μmol/mol) seen in central Nepal and France require as much as 97% Si loss from the initial fluid. Values of F_{Si} from 0.25 to 0.03 produce Ge/Si$_{fluid}$ ratios from 160 to 1100, indicating that modest changes in silica precipitation (such as caused by varying degrees of cooling and/or mixing with surface waters) can account for substantial variability within a given geothermal system. Precipitation of quartz from a cooling fluid probably occurs down to 75–50 °C; siliceous sinter precipitation at lower temperatures should have a similar effect on Ge/Si$_{fluid}$ (Arnorsson, 1984).

Polythermal equilibrium calculations were performed with Geochemists Workbench (Bethke, 1996) to test the feasibility of our Rayleigh model. An average central Nepal surface water was equilibrated and then reacted with a mineral assemblage similar to the host rocks of most of the springs (quartz, albite, microcline, muscovite, phlogopite [in place of biotite], and calcite) from surface temperatures of 15 to 250 °C. The fluid quickly reached saturation with quartz and remained saturated throughout the reaction. [Si] at 250 °C therefore reaches ~7000 μmol/kg (Fournier, 1985; Rimstidt, 1997). As the fluid is cooled along a polythermal path from 250 to 45 °C or quenched with cool surface waters, quartz precipitates, leaving the resultant fluid with [Si] $\cong$ 200 μM, a Si loss of ~97%. This value is in close agreement with the Si loss required for the Rayleigh model to produce very high Ge/Si$_{fluid}$ ratios (Fig. 2).

Himalayan springs with the highest Ge/Si ratios (500–1000 μmol/mol) are only 1.5–2.5 times supersaturated with quartz, whereas the springs with more moderate Ge/Si ratios (50–200 μmol/mol) are as much as 8 times supersaturated.

Supersaturation in hydrothermal fluids can result from kinetic inhibition of quartz nucleation or from mixing with surface waters (Fournier, 1985). Simple inhibition of quartz precipitation is essentially equivalent to increasing F_{Si}; a fluid moves back down the calculated Rayleigh curve as [Si] increases, and Ge/Si$_{fluid}$ ratios decrease. In contrast, mixing surface waters with hydrothermal fluids will cause fluid compositions to move below the modeled Rayleigh curve and toward much lower Ge/Si and low [Si] (i.e., toward the origin of Fig. 2). Surface waters in Nepal have Ge/Si < 1 and [Si] < 300 μM, similar to other regions. We suggest that mixing of hydrothermal fluid with surface waters plays a significant role in producing the observed variability in Ge/Si$_{fluid}$ ratios in a given hydrothermal system and in producing deviations from the idealized Rayleigh model behavior. Mixing surface water with hydrothermal fluids in various stages of evolution will produce a range of fluid Ge/Si and [Si] values in the region below the Rayleigh curve (Fig. 2) and can account for an important component of the variability.

The formation of secondary minerals other than quartz can affect the Ge/Si$_{fluid}$ behavior in hydrothermal systems. For example, the high-temperature submarine fluids are not well fit by the Rayleigh model, although quartz precipitation occurs in these systems. There is significant sulfide deposition from the high-temperature fluids (Bowers et al., 1985) and sulfides are known to be enriched in Ge (Bernstein, 1985). The precipitation of sulfide minerals will tend to lower Ge/Si ratios in the fluid phase and may be partly responsible for the relatively moderate Ge/Si ratios in fluids measured at axial hydrothermal vents.

CONCLUSIONS

Our models imply that the precipitation of quartz from thermal waters is the dominant control of the Ge/Si ratio in most thermal springs, and both models predict increasing Ge/Si$_{fluid}$ ratios with decreasing temperature. Quartz is a ubiquitous gangue mineral, and quartz solubility controls silica behavior in most hydrothermal systems (Fournier, 1985; Holland and Malinin, 1979), so our results should be widely applicable. Fluid equilibrium with an ideal solid-solution model for Ge in quartz successfully predicts Ge behavior at reservoir temperatures. A Rayleigh model of progressive precipitation of Ge-poor quartz predicts both the variability and, at low values of F_{Si}, the extreme Ge/Si$_{fluid}$ ratios seen in the central Nepal and Massif Central springs. Mixing of hydrothermal fluids with surface waters is another important source of variability. The low F_{Si} values are quantitatively consistent with reaction-path calculations for silica in this geothermal setting. The agreement between the degree of Si removal needed to produce the observed Ge/Si$_{fluid}$ ratios and the reaction-path modeling (for either simple cooling or surface-water mixing) suggests that Ge/Si ratios can be used to examine silica dynamics in hydrothermal systems and may be applicable to studies of scaling and silica deposition.

The thermal springs in central Nepal have high TDS values and in some cases deliver significant amounts of solutes to the river system (Evans et al., 2001). Assessing the impact that the central Nepal thermal springs have on the river system (e.g., river chemistry and fluxes of alkalinity and geothermal heat) depends on our ability to estimate spring fluxes. The wide disparity between Ge/Si ratios for surface waters (0.5 μmol/mol) and thermal waters (50–1000 μmol/mol) makes Ge/Si a valuable tool for quantifying the thermal springs discharge by chemical mass balance.

REFERENCES CITED

Arnorsson, S., 1984, Germanium in Icelandic geothermal systems: Geochimica et Cosmochimica Acta, v. 48, p. 2489–2502.

Balitsky, D.V., Balitsky, V.S., Pushcharovsky, D.Y., Bondarenko, G.V., and Kosenko, A.V., 1997, Growth and characterization of GeO$_2$ single crystals with the quartz structure: Journal of Crystal Growth, v. 180, p. 212–219.

Bernstein, L.R., 1985, Germanium geochemistry and mineralogy: Geochimica et Cosmochimica Acta, v. 49, p. 2409–2422.

Bethke, C.M., 1996, Geochemical reaction modeling: New York, Oxford University Press, 397 p.

Bowers, T.S., Von Damm, K.L., and Edmond, J.M., 1985, Chemical evolution of midocean ridge hot springs: Geochimica et Cosmochimica Acta, v. 49, p. 2239–2252.

Capobianco, C., and Navrotsky, A., 1982, Calorimetric evidence for ideal mixing of silicon and germanium in glasses and crystals of sodium-feldspar composition: American Mineralogist, v. 67, p. 718–724.

Criaud, A., and Fouillac, C., 1986, Study of CO$_2$-rich thermomineral waters from the central French massif. 2. Behavior of some trace-metals, arsenic, antimony and germanium: Geochimica et Cosmochimica Acta, v. 50, p. 1573–1582.

Evans, M.J., Derry, L.A., Anderson, S.P., and France-Lanord, C., 2001, Hydrothermal source of radiogenic Sr to Himalayan rivers: Geology, v. 29, p. 803–806.

Fournier, R.O., 1985, The behavior of silica in hydrothermal systems, in Berger, B.R., and Bethke, P.M., eds., Geology and geochemistry of epithermal systems: Society of Economic Geologists Reviews in Economic Geology, v. 2, p. 45–62.

Froelich, P.N.V., Blanc, R.A., Mortlock, R.A., Chillrud, S.N., Dunstan, W., Udomkit, A., and Peng, T.-H., 1992, River fluxes of dissolved silica to the ocean were higher during glacials: Ge/Si in diatoms, rivers, and oceans: Paleoceanography, v. 7, p. 739–767.

Galy, A., and France-Lanord, C., 1999, Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget: Chemical Geology, v. 159, p. 31–60.

Grabczak, J., and Kotarba, M., 1985, Isotopic composition of the thermal waters in the central part of the Nepal Himalayas: Geothermics, v. 14, p. 567–575.

Holland, H.D., and Malinin, S.D., 1979, The solubility and occurrence of nonore minerals, in Barnes, H.L., ed., Geochemistry of hydrothermal ore deposits, Volume 1: New York, John Wiley and Sons, Inc., p. 461–508.

Johnson, J.W., Oelkers, E.H., and Helgeson, H.C., 1992, SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0–1000 °C: Computers and Geosciences, v. 18, p. 899–947.

Kurtz, A., Derry, L.A., and Chadwick, O.A., 2002, Germanium-silicon fractionation in the weathering environment: Geochimica et Cosmochimica Acta, v. 66, p. 1525–1537.

Martin, F, Ildefonse, P., Hazemann, J.L., Petit, S., Grauby, O., and Decarreau, A., 1996, Random distribution of Ge and Si in synthetic talc: An EXAFS and FTIR study: European Journal of Mineralogy, v. 8, p. 289–299.

Mortlock, R.A., and Froelich, P.N., 1987, Continental weathering of germanium-Ge/Si in the global river discharge: Geochimica et Cosmochimica Acta, v. 51, p. 2075–2082.

Mortlock, R.A., and Froelich, P.N., 1996, Determination of germanium by isotope dilution hydride generation inductively coupled plasma mass spectrometry: Analytica Chimica Acta, v. 332, p. 277–284.

Mortlock, R.A., Froelich, P.N., Feely, R.A., Massoth, G.J., Butterfield, D.A., and Lupton, J.E., 1993, Silica and germanium in Pacific Ocean hydrothermal vents and plumes: Earth and Planetary Science Letters, v. 119, p. 365–378.

Murnane, R.J., and Stallard, R.F., 1990, Germanium and silicon in rivers of the Orinoco drainage basin: Nature, v. 344, p. 749–752.

O'Neill, H.S.C., 1986, Standard molar Gibbs free-energies of formation of the tetragonal and hexagonal forms of germanium dioxide: Journal of Chemical Thermodynamics, v. 18, p. 465–471.

Pokrovski, G.S., and Schott, J., 1998, Thermodynamic properties of aqueous Ge(IV) hydroxide complexes from 25 to 350 °C: Implications for the behavior of germanium and the Ge/Si ratio in hydrothermal fluids: Geochimica et Cosmochimica Acta, v. 62, p. 1631–1642.

Rimstidt, J.D., 1997, Quartz solubility at low temperatures: Geochimica et Cosmochimica Acta, v. 61, p. 2553–2558.

Royden, L.H., 1993, The steady-state thermal structure of eroding orogenic belts and accretionary prisms: Journal of Geophysical Research, v. 98, p. 4487–4507.

Smith, G.S., and Isaacs, P.B., 1964, Crystal structure of quartz-like GeO$_2$: Acta Crystallographica, v. 17, p. 842–846.

Stefansson, A., 2001, Dissolution of primary minerals of basalt in natural waters: I. Calculation of mineral solubilities from 0 °C to 350 °C: Chemical Geology, v. 172, p. 225–250.

Tanger, J.C., and Helgeson, H.C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes: American Journal of Science, v. 288, p. 19–98.