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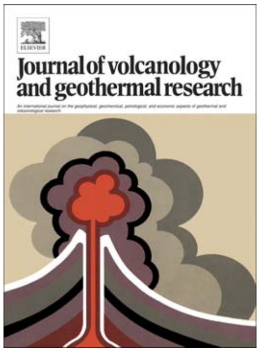

Towards understanding the puzzling lack of acid geothermal springs in Tibet (China): Insight from a comparison with Yellowstone (USA) and some active volcanic hydrothermal systems

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Towards understanding the puzzling lack of acid geothermal springs in Tibet (China): insight from a comparison with Yellowstone (USA) and some active volcanic hydrothermal systems

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Abstract: Explanations for the lack of acid geothermal springs in Tibet are inferred from a comprehensive hydrochemical comparison of Tibetan geothermal waters with those discharged from Yellowstone (USA) and two active volcanic areas, Nevado del Ruiz (Colombia) and Miravalles (Costa Rica) where acid springs are widely distributed and diversified in terms of geochemical characteristic and origin. For the hydrothermal areas investigated in this study, there appears to be a relationship between the depths of magma chambers and the occurrence of acid, chloride-rich springs formed via direct magmatic fluid absorption. Nevado del Ruiz and Miravalles with magma at or very close to the

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surface (less than 1-2 km) exhibit very acidic waters containing HCl and H_2SO_4. In contrast, the Tibetan hydrothermal systems, represented by Yangbajain, usually have fairly deep-seated magma chambers so that the released acid fluids are much more likely to be fully neutralized during transport to the surface. The absence of steam-heated acid waters in Tibet, however, may be primarily due to the lack of a confining layer (like young impermeable lavas at Yellowstone) to separate geothermal steam from underlying neutral chloride waters and the possible scenario that the deep geothermal fluids below Tibet carry less H_2S than those below Yellowstone.

Key words: geothermal water; geochemistry; acid spring; magma chamber; steam-heating; Tibet; Yellowstone; active volcanic-hydrothermal area

1. Introduction

Tibet, with a total area of 1,228,400 km^2, is the region in mainland China where high-temperature hydrothermal systems are most widely and intensively distributed (Fig. 1-a). According to the estimations based upon chemical geothermometers, there are 129 and 12 hydrothermal systems in Tibet with reservoir temperature higher than 150 and 200 °C respectively (Liao and Zhao, 1999). The most striking geochemical characteristics of the Tibet hydrothermal systems is that acid springs have not been found so far there, which is different from most high-temperature hydrothermal areas across the world. Tong et al. (2000) made a systematic survey of Tibet geothermal springs, but recorded only three springs with pH values lower than 5.5 (4.5, 5.0 and 5.0 respectively) (Fig. 2). In fact, even

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in the Yangbajain geothermal field of Tibet where 34 production wells with depths from ~200 m to 1850 m were drilled, the waters extracted from all these boreholes are still neutral-chloride waters (Duo, 2003; Guo et al., 2007). The neutral waters from some of Tibet hydrothermal systems, however, are characterized by quite high sulfate concentrations (Fig. 2). In Tibet, it is not unusual that neutral but sulfate-rich geothermal waters are hosted by igneous rocks (Tong et al., 1981). Yangyi and Langjiu are typical granite-hosted hydrothermal systems in Tibet discharging neutral, sulfate-rich waters (Guo et al., 2009; Tong et al., 2000).

Despite the uncommon lack of acid springs in Tibetan hydrothermal areas, there are so far no literatures presenting the intrinsic factors responsible for this fact. Hence, ***the main aim of this study is to clarify the geochemical genesis for the absence of acid springs in Tibet by comparing Tibet geothermal waters with those from Yellowstone National Park (USA) primarily and two active volcanic hydrothermal systems (Nevado del Ruiz, Colombia and Miravalles, Costa Rica) subordinately***. The primary reason for the selection of Yellowstone for the comparison is that the Yellowstone geothermal waters have a much wider pH range (Fig. 2) and acid geothermal springs are widely distributed there (with measured field pH values as low as 1 - 2) (Nordstrom et al., 2009). Since the acid waters discharged from Yellowstone are essentially steam-heated waters (i.e. locally-perched groundwaters heated by H_2S-rich steam separated from deep geothermal fluid) or their mixtures with neutral chloride waters to different degrees, Nevado del Ruiz and Miravalles are used for the comparison with Tibetan hydrothermal areas as well, in view that the acid

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springs from these two systems are formed due to the direct absorption of magmatic fluid by infiltrating waters, which are substantially different from Yellowstone acid springs in terms of geochemical genesis.

2. Comparison between Tibet and Yellowstone in terms of geographical and geological settings as well as selection of hydrothermal sites

There are some similarities shared by Tibet and Yellowstone. Both of them are well within large continental land masses and located on high plateaus with abundant precipitation. Yellowstone averages about 2600 m in elevation and Tibet averages over 4000 m. Both have magmatic heat sources and are marked with numerous and widespread boiling springs with known or inferred reservoir temperatures exceeding 300 °C.

Tibet differs from Yellowstone in some aspects as well. Besides the lack of acid springs, another important characteristic differentiating Tibet from Yellowstone and active volcanic hydrothermal areas is that no evidence exists for the occurrence of Late-Cenozoic volcanic eruptions within the high-temperature hydrothermal areas of Tibet. All twelve volcanoes erupted in and around Tibet during the Late Cenozoic are located very near to the border between Tibet and Xinjiang (Tong et al., 1990), far away from the Tibetan hydrothermal areas (Fig. 1-a). In comparison, the last volcanic eruption at Nevado del Ruiz and Miravalles occurred about 30 and 7,000 years ago respectively. In Yellowstone, volcanism with a total area of around 9,000 km^2 has lasted for 2.2 Ma with the latest rhyolitic lava eruption being around 70,000 ago (Fournier, 1989). The Yellowstone

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hydrothermal areas are just located in or within close proximity to a large-scale caldera formed around 0.6 Ma ago (Fig. 1-b).

In order to account for the lack of acid geothermal waters in Tibet, a selection process was necessary to focus this study on those geothermal water samples for which the major lithologies and geologic features had been determined, the hydrochemical data were adequate (major ions and selected trace elements had been determined), and the quality of hydrochemical analyses was reliable. This section describes primarily the background geology and the selection process.

2.1. Tibet hydrothermal systems

There are 191 known hydrothermal areas in Tibet, of which 44 areas have springs with temperatures at the boiling point of water for their elevation (Tong et al., 2000). For all these areas, 269 water samples with reliable chemical analyses are available. Thermal features are designated based on whether water temperature is greater than the local mean annual air temperature. In view that average annual air temperature in the Tibetan plateau is very low (usually around or even lower than 0 °C), 26 geothermal water samples have temperatures less than 25 °C.

There is a lack of detailed geological and geophysical studies for most of the high-temperature hydrothermal areas, although Tong and others made a series of surface geothermal investigations and collected geothermal water samples across Tibet in the 1970s and 1980s (Tong et al., 2000). Boreholes for geological survey or geothermal production

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have been drilled in only four hydrothermal areas of Tibet: i.e. Yangbajain, Yangyi, Langjiu and Nakqu, with the maximum depths of 1850 m, 953 m, ~100 m and 708 m respectively. Moreover, systematic geophysical surveys have been carried out in Yangbajain and Yangyi as well.

In this study, Yangbajain, Gudui, Yangyi and Langjiu were chosen as representative hydrothermal areas of Tibet. The geothermal waters discharged from Yangbajain and Gudui are neutral chloride waters with low sulfate concentrations, whereas those from Yangyi and Langjiu are neutral waters enriched in bicarbonate, sulfate and chloride with bicarbonate dominant in some of them. Among these hydrothermal areas, Yangbajain and Yangyi were investigated systematically in the past three decades (Japan International Collaboration Agency and Tibet Electric Power Company, 2006; Cai et al., 1986; Duo, 2003; Guo et al., 2007; Guo et al., 2009; Liao and Zhao, 1999; Shen, 1986; Tong et al., 1981; Zhao et al., 1998b), and the existence of a magmatic heat source and high-temperature reservoir (over 200 °C) has been confirmed for both of them. The highest measured borehole temperature at Langjiu is only 105 °C because the depths of all boreholes there are shallow (~100 m), but it was still selected in view that its background geology has been partially disclosed from drilling and the reservoir temperatures estimated by use of geothermometers are higher than 200 °C. The reason for the selection of Gudui is that it is characterized by the most intensive hydrothermal activity among all Tibet geothermal areas. Although we know little about the reservoir lithology beneath Gudui and there is no direct evidence for the existence of magma chamber (no drilling and geophysical work were made in Gudui),

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Gudui is very much likely to be a magmatic hydrothermal system in view of its hydrochemistry very similar to Yangbajain. Nakqu is not considered though it is one of four hydrothermal areas in Tibet where the geological background has been clarified on the basis of borehole data. Thirty-eight boreholes were drilled in the Nakqu hydrothermal area with the greatest depth up to 953 m (Tong et al., 2000), but the highest measured subsurface temperature below Nakqu is only 116 °C. Thus, Nakqu might not be heated by a magma chamber, and therefore are not comparable with other magmatic-hydrothermal areas investigated in this study.

The geological and geothermal characteristics of Yangbajain, Gudui, Yangyi and Langjiu are summarized in Table 1 and Supplementary Materials. The basic information and chemical compositions of the water samples collected from these hydrothermal areas are presented in Tables S1 and S2.

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2.2. Yellowstone and other hydrothermal systems

Yellowstone National Park, located largely in the northwestern part of Wyoming (USA) and marked with unparalleled hydrothermal activity, is the largest geothermal region in the world. More than 10,000 thermal features are compiled in a database by the National Park Service (Rodman and Guiles, 2008). There were three gigantic caldera-forming eruptions of silicic pyroclastics around 2.0, 1.3 and 0.6 Ma ago respectively, before and after each of which large-scale eruptions of rhyolitic and basaltic lava were emplaced (Fournier, 1989). Within and around the 0.6 Ma caldera, the Yellowstone reservoirs are hosted by rhyolite

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lava flows or ash-flow tuffs with relatively uniform chemical composition, the predominant rock being the Plateau Rhyolite (Christiansen, 2001). In addition, the existence of an active magmatic system with depths of about 8-10 km beneath the 0.6 Ma Yellowstone caldera has been indicated by various geological and geophysical observations (Blank and Gettings, 1974; Chu et al., 2010; Lehman et al., 1982; Husen et al., 2004; Bhattacharyya and Leu, 1975; Benz and Smith, 1984; Chang et al., 2010; Pierce and Morgan, 2009; Smith et al., 2009). Based on chemical geothermometers and curves of theoretical boiling-point versus depth for hydrostatic conditions, it was estimated that hydrothermal fluids last equilibrate at depths of 100 to 550 m with temperatures ranging from around 180 to 270 °C (Fournier et al., 1976).

The geological settings for most hydrothermal areas in Yellowstone are well documented. One of the criteria for selection of Yellowstone geothermal water samples was that those hydrothermal systems hosted by sedimentary rocks outside the 0.6 Ma caldera are excluded (e.g. the Mammoth Hot Springs area, Washburn area, Hot Spring Basin, Rainbow Springs, and other springs in the northeast corner of the Park); that is, all the selected samples were collected from volcanic rock-hosted hydrothermal systems and most of them are within the 0.6 Ma caldera. These hydrothermal areas comprise Nymph Lake area, West Nymph Creek Thermal Area, Norris Geyser Basin, Gibbon Geyser Basin, Crater Hills, Mud Volcano, Lower Geyser Basin, Midway Geyser Basin, Upper Geyser Basin, Potts Hot Spring Basin, and West Thumb Geyser Basin (Fig. 1-b). Basically, those samples which can be regarded as representatives of chemical end-members are chosen (i.e. neutral

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chloride waters with low sulfate concentrations and acid sulfate waters with low chloride concentrations), although some intermediate types of water samples are also used. The details of Yellowstone water samples are given in Tables S1 and S2.

Nevado del Ruiz in Colombia and Miravalles in Costa Rica are selected as the representative volcanic-magmatic-hydrothermal systems, with eight acid water samples and ten neutral water samples from there (Giggenbach et al., 1990; Giggenbach and Soto, 1992) being used for this study (Tables S1 and S2). Selection of these samples provides water chemistry data for very shallow magmatic systems to compare with the deep systems in Tibet and the systems with intermediate depths at Yellowstone. As mentioned earlier, the chemistry of strongly acid discharges from Nevado del Ruiz and Miravalles are affected by the direct contribution of magmatic fluids due to their shallow depths (Giggenbach et al., 1990; Giggenbach and Soto, 1992).

3. Sample collection and analysis

Geothermal waters from Tibet and Yellowstone sampled by the authors of this paper were filtered and preserved on site, as described by Guo et al. (2009), McCleskey et al. (2005, 2014) and Ball et al. (2006, 2010). They were collected in polyethylene bottles, which had been soaked in 5% HCl and rinsed three times with distilled water before collection. For cation analysis, reagent-grade, concentrated, redistilled HNO_3 was added to one sample collected at each site to bring pH below 1. Samples for SiO_2 analysis were diluted using deionized water to prevent SiO_2 precipitation. Sample splits for analyses of anions were stored with no chemical agents added. Similar collection and preservation

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methods were used for the Tibetan water samples collected by other investigators and documented in Tong et al. (2000) and Japan International Collaboration Agency and Tibet Electric Power Company (2006).

For the water samples collected from Tibet and Yellowstone, measurements of pH and water temperature were performed on-site and alkalinity was measured using the Gran titration method. A variety of analytical techniques were used for measurements of major anions (SO_4^{2-}, Cl^-, F^- and Br^-), cations (Na, K, Ca, Mg, Li, Rb and Cs) and other constituents (As, B, SiO_2, Al, Fe, H_2S and NH_4^+) in geothermal water, as summarized in Table 2 and reported by Guo et al. (2009), Tong et al. (2000), Japan International Collaboration Agency and Tibet Electric Power Company (2006), McCleskey et al. (2005, 2014) and Ball et al. (2006, 2010). Analyses of the Tibet and Yellowstone waters were screened based on major ions and important geothermal solutes; any analyses lacking too many ions were excluded. All analyses were also screened in terms of charge balance. No samples with > 15% charge imbalance were used in this study (commonly less than 10 %).

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4. Results and discussion

4.1. Hydrochemical characteristics of geothermal samples

4.1.1. pH values and chloride and sulfate concentrations

The water samples from selected Tibet hydrothermal systems are all pH neutral as elsewhere in Tibet, but have a wide range of sulfate concentrations (8.4 - 388 mg/L). The Yangbajain and Gudui samples are neutral-chloride waters with low sulfate concentrations,

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whereas the Yangyi and Langjiu samples are enriched in bicarbonate, sulfate and chloride with bicarbonate dominant in some of them.

In contrast, the neutral Yellowstone samples are all chloride waters with low sulfate concentration and comparable to the Tibet samples in terms of chloride concentration, and the acid Yellowstone samples have wide ranges of sulfate and chloride concentrations (Fig. 3-a and 3-b). The acid geothermal waters from Yellowstone can be further divided into two different types: 1) acid waters with extremely high sulfate but low chloride concentrations, and 2) acid waters with moderate sulfate and chloride concentrations. Correspondingly, type 1 acid waters have highest SO_4/Cl molar ratios and lowest pH values among all Yellowstone samples, whereas type 2 acid waters have much lower SO_4/Cl ratios and more scattered pH values as compared to type 1 (Fig. 3-c). It is noteworthy that the trend in SO_4/Cl ratio with pH suggests a mixing process for the Yellowstone samples as indicated by the dashed line (Fig. 3-c). Indeed, mixing of acid-sulfate waters with neutral-chloride waters in some Yellowstone hydrothermal areas is a common phenomenon, e.g. the Norris Geyser Basin (Fournier et al., 2002; Nordstrom et al., 2009).

As compared to Yellowstone acid waters, those acid geothermal waters from Nevado del Ruiz (Colombia) and Miravalles (Costa Rica) generally have higher chloride and sulfate concentrations. The chemical characteristics of these brines are typical for active volcanic environments (Giggenbach, 2003; Giggenbach et al., 2003).

4.1.2. Sodium and potassium concentrations

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The Na concentrations of the geothermal waters from Tibet and Yellowstone are comparable, but much lower than those of most neutral waters from active volcanic areas (Fig. 4-a). The comparison of K concentration in geothermal water among different areas is somewhat similar to Na. The circumneutral geothermal waters from Miravalles have higher K concentrations than the Tibet and Yellowstone waters, whereas the acid waters from active volcanic areas are characterized by a much wider K concentration range (Fig. 4-b). Moreover, it is worth noting that the Sulphur Spring, a moderately acidic spring discharged from the Crater Hills area of Yellowstone, has remarkably higher K concentration than the other Yellowstone samples. In fact, this spring is also characterized by the highest Cl and Na concentrations as well as estimated subsurface temperatures among all Yellowstone springs, and therefore is considered to be a representative of the most direct upflow of deep fluid at Yellowstone (Fournier, 1989). The Sulphur Spring is highly boiled, and its acidity should come from a small addition of acid sulfate water. Thus, its elevated K concentration is due to either extensive subsurface boiling or the possibility that it has not lost as much K via precipitation of illite as neutral chloride waters.

The geothermal water samples used in this study (except for some acid waters from active volcanic areas) generally have Na/Cl molar ratios close to or higher than unity (Fig. 4-a), demonstrating that Na is the dominant cation in chloride-rich geothermal waters, as observed elsewhere across the world. A further inspection in the Na/Cl molar ratios of the Tibet and Yellowstone geothermal waters shows that some neutral water samples, especially those from Yangyi and Langjiu, have a range of Na at almost constant Cl (Fig.

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4-a). The surplus Na to varied degrees in these samples should be caused by hydrogen metasomatism as a result of the attack of CO_2 on rocks at near-surface environments as Giggenbach (1988) proposed. That is, during the ascent of deep CO_2-bearing geothermal fluids to surface, the decrease in environmental temperature and pressure results in a rapid increase in the reactivity of CO_2, which in turn induces its reaction with host rocks and subsequent transformation to HCO_3 or CO_3. This possibility is confirmed by a plot of Na/Cl milliequivalent ratio versus $(HCO_3+CO_3)/Cl$ milliequivalent ratio for the neutral samples from Tibet and Yellowstone (Fig. 4-c). The samples that are most variant from the 1:1 molar ratio line in Fig. 4-a (from Yangyi and Langjiu) are those with the highest $(HCO_3+CO_3)/Cl$ ratios.

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4.1.3. Calcium and magnesium concentrations

The situation for Ca and Mg is opposite to that for Na and K. The Ca concentration of geothermal water is affected by its acidity because of the pH control on solubility of Ca-bearing minerals (especially carbonate minerals). In this study, the acid geothermal waters, regardless of their sampling locations, generally have higher Ca and Mg concentrations than neutral geothermal waters. The Ca and Mg concentrations of sulfate-rich neutral waters from Tibet are higher than those of sulfate-depleted waters (Fig. 5-a and 5-b). Moreover, the geothermal waters from Yangbajain production wells have much lower Ca and Mg concentrations than those from Yangbajain geothermal springs, probably because the latter have been affected strongly by the mixing of Ca- and Mg-rich

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local cold groundwaters. The extremely low Mg concentrations (as low as <0.01 mg/L) are one of the most sensitive characteristics for distinguishing typical neutral chloride waters from acid sulfate waters (Fig. 5-b). This characteristic is more clearly demonstrated in Fig. 5-c where Mg/Cl ratio has been plotted against pH value and the samples with pHs less than 4.5 are designated separately from those with higher pH values. Low pH samples (< 4.5) have consistently higher Mg/Cl ratios except for 7 Yellowstone samples that are mixtures of acid waters with enough neutral chloride waters so that their Mg/Cl ratios have been lowered to the same range as the neutral waters.

4.2. Geochemical geneses for geothermal waters from different systems

For a typical volcanic-magmatic-hydrothermal system with magmatic heat source, three different types of hot springs are usually identified: acid SO_4-Cl or Cl-SO_4 spring (enriched with both SO_4 and Cl), neutral Cl spring, and slightly alkaline to neutral HCO_3-Cl spring (Giggenbach, 1988). Within such systems, release of magmatic fluid and its subsequent mixing with infiltrating waters results in the formation of highly immature waters characterized by very high SO_4^{2-} and Cl^- concentrations and very low pH values. The interactions between these immature acid waters and rocks, also called primary neutralization process, can produce neutralized Cl waters during which magmatic sulfur is partly incorporated into alunite, anhydrite or pyrite at different depths. As neutralized Cl waters ascend, they boil to form a two-phase vapor-water flow. The separated vapor is usually CO_2-rich and its reactivity can be enhanced due to temperature decrease along the

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flow path of geothermal fluid. The conversion of dissolved CO_2 in neutral Cl waters to HCO_3^- through interaction with host rocks at comparatively shallow levels may generate HCO_3-Cl waters or even HCO_3 waters (Giggenbach, 1988).

Some volcanic vapor condensates, e.g. those collected by Goff and McMurtry (2000) from active volcanoes (Pacaya, Satsuma Iwo-Jima, Galeras, Kudryavy, Kilauea, etc.), can be regarded as the representatives of "comparatively pure magmatic fluid" that were affected by mixing of meteoric waters or by reaction with subsurface rocks to a very limited degree, in view of their extremely low pH values, very high SO_4^{2-} and Cl^- concentrations, and very low concentrations of major metal elements including Na, K, Ca and Mg. The acid geothermal waters from Nevado del Ruiz and Miravalles, very close to these volcanic vapor condensates in terms of pH value as well as SO_4^{2-} and Cl^- concentrations but marked with much higher Na, K, Ca and Mg concentrations, are basically the result of isochemical dissolution of subsurface rocks by magmatic fluids (Giggenbach et al., 1990; Giggenbach and Soto, 1992). They are still acidic because considerable H^+ has not been consumed by rock dissolution. Thus, the Nevado del Ruiz and Miravalles acid waters just experienced very incomplete neutralization processes.

The geochemical geneses for various types of acid waters from Yellowstone are complex and diverse. The acid Yellowstone geothermal springs with low Cl and Na concentrations (Type 1) were formed via uptake of steam, rich in H_2S, by dilute surface and near-surface meteoric waters (Nordstrom et al., 2009), which is distinctively different from those chloride-rich acid waters from active volcanic areas. These two kinds of acid waters,

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corresponding to so-called “low sulfidation” and “high sulfidation” and responsible for the formation of hydrothermal ore deposits, were also discussed by Hedenquist and Lowenstern (1994). During the boiling process of a geothermal fluid, Cl and Na remain in the liquid phase, and therefore their concentrations in steam-heated springs are quite low. However, the flash steam usually contains a great deal of H_2S, which can be oxidized to SO_4^{2-} at near-surface groundwater environments (often aided by microbial catalysis) to produce acidity in steam-heated waters. This explanation for the occurrence of low-chloride acid geothermal waters in Yellowstone is also supported by geophysical evidence. The Norris Geyser Basin, located in the northwestern part of the Yellowstone volcanic rock area, is one of the areas where type 1 acid springs are distributed most intensively. A seismic study made by Husen et al. (2004) indicates that a volume of anomalously low P-wave velocity and P-wave to S-wave velocity ratio exists just in this part of Yellowstone with very shallow depths of less than 2.0 km. This anomaly is a reflection of porous, gas-filled rock, and the gas should originate from the adiabatic cooling of deep geothermal fluids (Husen et al., 2004).

In contrast, those acid Yellowstone geothermal waters with lower SO_4-Cl molar ratios because of their elevated Cl concentrations (i.e. Type 2) are the result of mixing between type 1 acid waters and neutral chloride waters. A typical representative of type 2 Yellowstone acid waters is the “Crystal Sister East” Spring in the Norris Geyser Basin. The pH value and chemical composition of this spring change a lot over time on account of the variation of mixing ratios of its two end-members (Fig. 6). In general, as compared to the

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chloride-rich acid waters from active volcanic areas formed by immediate absorption of magmatic fluids, all Yellowstone acid samples have much lower Cl or SO_4 concentrations, and therefore have no direct relation to contribution of magmatic fluid.

Neutral chloride waters are common for most high-temperature, felsic-rock-hosted hydrothermal systems including those located in active volcanic areas. For a high-temperature system with magmatic heat source, neutral geothermal waters with Cl as a dominant anion is usually considered to be the result of full neutralization of magmatic fluid (Giggenbach, 1988). This hypothesized process can be divided into two phases: (1) isochemical rock dissolution, i.e., the addition of metals including Na, K, Mg and Ca to the geothermal fluid in proportions very close to those of the original rocks; (2) formation of secondary altered minerals, which mainly involves precipitation of Mg- and Ca-rich alteration products (such as biotite, chlorite, calcite, anhydrite and fluorite) and incorporation of magmatic sulfur to alunite, anhydrite or pyrite at different depths (Giggenbach, 1988). Only after complete interactions between acid magmatic fluids and rocks, Cl-enriched but SO_4-, Ca- and Mg-depleted waters could be formed, which are represented by the Yangbajain and Gudui geothermal waters in this study. Those neutral chloride springs from Yellowstone, Nevado del Ruiz and Miravalles belong to this type as well.

4.3. Equilibrium status of geothermal waters with regards to reservoir minerals

By use of Giggenbach's Na-K-$Mg^{1/2}$ diagram, the geochemical differences among the

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geothermal waters from selected hydrothermal systems can be illustrated by their equilibrium status with regard to a thermodynamically stable mineral assemblage including albite, K-feldspar, muscovite (thermodynamic proxy for illite) and clinochlore (thermodynamic proxy for chlorites). The general disequilibrium situation for all acid geothermal water samples, no matter where they were collected from, is clearly documented by the Na-K-Mg$^{1/2}$ diagram (Fig. 7). Most acid samples are located in the immature water area, with some of them falling in the partially equilibrated area. In contrast, quite a few neutral chloride water samples with low sulfate concentrations, especially those collected from geothermal production wells (Yangbajain and Miravalles), are located on or closely around the full equilibrium line. It is worth noting that some neutral waters from Yellowstone lie beyond the equilibrium line, implying that these samples have fully equilibrated with the above mineral assemblage until they were discharged to surface, but then experienced strong surface evaporation upon discharge. Hence, their K-Mg temperatures become higher than their Na-K temperatures. As compared to the geothermal well samples, the Yangyi and Langjiu samples enriched in sulfate are further away from the equilibrium line, possibly as a result of partial neutralization of magmatic fluids. However, this possibility is slim (at least for Yangyi) in view that the magmatic heat source below Yangyi is fairly deep (9 - 15 km). An alternative explanation is that they may somehow be affected by the mixing of shallow groundwaters and their high sulfate concentrations are of sedimentary origin (sediments beneath or adjacent to the exposed igneous rocks), although it needs to be further validated by more evidence, e.g. S and O isotope data for the sulfate

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in geothermal waters. Moreover, some neutral chloride water samples with low sulfate concentrations are also located in the partially equilibrated area or even the immature water area. Further inspection indicates that all of these samples were collected from the Yangbajain springs before the construction of geothermal power plants there. Thus, the elevated Mg concentrations of these geothermal waters are very likely due to dilution by local Mg-rich groundwaters or quick acquisition of Mg from subsurface rocks in response to decreasing temperatures during their ascent all the way to the surface.

Although Li, Rb and Cs analyses are available only for a limited subset of the samples, a Li-Rb-Cs ternary diagram of all these water samples was prepared (Fig. 8) for appraising their equilibrium status as well. In Fig. 8, the very acid waters from Yellowstone and active volcanic areas plot closely around a solution resulting from isochemical dissolution of an average crustal rock (marked as “rock” surrounded by a circle), demonstrating that they are far from being fully equilibrated with thermodynamically stable minerals. In contrast, all neutral geothermal water samples have much lower Rb concentrations as compared to rock-dissolution, implying the removal of Rb from water. Potassium-rich aluminum silicates, e.g. illite, can easily precipitate from geothermal water having undergone isochemical dissolution process. Because Rb has very similar geochemical behavior to K, it can also be preferentially taken up by illite formed at considerable depth and relatively high temperatures. Thus, neutral geothermal waters lose most of their original Rb during neutralization. In contrast to Rb, Cs tends to remain in solution after its dissolution from rock and can only be incorporated into secondary zeolites at lower temperatures, while Li

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can be removed via precipitation with secondary quartz, micas (lepidolite), or chlorite. Fig. 8 portrays the removal of Li by secondary silicate minerals for the Tibetan waters, whereas the precipitation of Cs can be expected for the Yellowstone waters. As compared to the neutral Yellowstone samples, Sulphur Spring is closer to the Rb apex, indicating once again that less illite is precipitated from the geothermal waters feeding this spring as compared to neutral chloride springs from Yellowstone.

4.4. Possible factors responsible for the lack of acid geothermal springs in Tibet

4.4.1 Lack of acid springs formed through direct uptake of magmatic fluid

The formation mechanisms of magmatic heat source for the high-temperature hydrothermal systems in Tibet and Yellowstone are substantially different. The Tibet hydrothermal systems are mostly located along the border between the Eurasian and Indian plates. The collision between these two plates resulted in the remelting of strata composed of marine sedimentary rocks, which in turn caused the formation of numerous magma chambers that drive the thermal flux in southern Tibet. That is, partial melting of sialic sedimentary rocks during crustal thickening and orogeny in Tibet is the most possible mechanism for the formation of magmas beneath Tibetan hydrothermal systems. Hence, they are very likely to be of a granitic composition, distinctively different than the basaltic intrusions in rift zones and hot spots across the world (Brown et al., 1996). The above hypothesis is supported by the extremely high terrestrial heat flow, widely distributed hydrothermal areas, and the tectonic background of Tibet. It matches well with other

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geophysical observations by the INDEPTH project conducted in the 1990s as well (Chen et al., 1996; Kind et al., 1996; Makovsky et al., 1996; Nelson et al., 1996). In contrast, it is commonly accepted that Yellowstone is a hotspot, and therefore the driving thermal force at Yellowstone is a localized upflow of silicic magmas. These basic differences in tectonic environment are hypothesized to cause some dissimilarity in hydrothermal chemistry between Tibet and Yellowstone (or active volcanic hydrothermal systems).

Thus, the magma chambers beneath Tibetan geothermal areas are fairly deep-seated so that the acid, chloride-rich fluids released from these magmas have been fully neutralized during their reactions with host rocks and their mixing with infiltrating groundwaters. Yangbajain is representative of the Tibet hydrothermal systems with deep magma chamber as heat source. The magma chamber below the Yangbajain geothermal field, as suggested by the geophysical investigations of INDEPTH project, is at depths of 15-18 km. Consequently, the geothermal waters discharged from all hot springs and geothermal wells at Yangbajain are neutral chloride waters with low sulfate concentrations. At Yellowstone, the depths of magma are generally about 8-10 km, and therefore the released fluids have been neutralized in most hydrothermal areas as well. All Yellowstone acid springs are either steam-heated local groundwaters or the results of their mixing with neutral chloride waters as discussed earlier. However, as compared to Tibetan systems, those hydrothermal systems in active volcanic areas, e.g. Nevado del Ruiz and Miravalles, have much shallower magmatic heat sources. The magma chambers below these systems are very close to the surface with depths less than 1-2 km (Giggenbach et al., 1990; Giggenbach and Soto, 1992).

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Correspondingly, very acid SO_4-Cl or Cl-SO_4 waters occur commonly at Nevado del Ruiz and Miravalles, and their SO_4^{2-} and Cl^- concentrations are generally higher than those of the Yellowstone acid springs. At least in portions of these two systems (as well as in other active volcanic hydrothermal areas of the world), the magmatic fluids have been little neutralized until they were discharged to the surface. To conclude, shallow magma is necessary for a hydrothermal system to form acid springs with HCl component, although not all hydrothermal systems with shallow magma chambers discharge acid springs (a good example is the Mount St. Helens Crater (USA) where magma was even extruding out to form a dome while the crater springs had near neutral pHs and acid sulfate springs were not found there). In Tibet, the lack of acid springs formed through direct uptake of magmatic fluid is primarily due to the very deep magmas below hydrothermal systems.

4.4.2 Lack of acid springs formed through geothermal steam heating

The deep-seated magma chambers below Tibetan hydrothermal areas are considered to be responsible for the lack of acid geothermal springs enriched in both sulfate and chloride that are directly linked to magmatic fluid. However, it seems to be puzzling that acid, steam-heated, sulfate waters occurring in shallow perched aquifers (without a direct relation to magmatic fluid and formed via near-surface oxidation of H_2S separated from neutral geothermal fluid), which are common at Yellowstone, are absent in Tibet as well.

It has been observed that neutral Yellowstone geothermal springs often come out at formation boundaries with comparatively low elevations, such as Upper Geyser Basin,

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Lower Geyser Basin and West Thumb. Acid steam-heated springs at Yellowstone, however, were usually found on the tops of unfractured lava caps. That is, young lava flows, erupting and covering old geothermal areas at Yellowstone 150,000 to 100,000 years ago, act to separate neutral and acid waters (Hurwitz et al., 2007; Lowenstern and Hurwitz, 2008; Morgan et al., 2005; White, 1957). Underneath the lava flows, the neutral geothermal fluids flow laterally and are discharged in the “current” geyser basins at Yellowstone. These neutral waters may boil as they flow to generate H_2S-rich steams that rise from a few discrete points along the flow path (basically permeable faults or fractures) and then form steam-heated, sulfate-rich waters at higher elevations. In fact, besides Yellowstone, many other hydrothermal systems related to stratovolcanoes discharging steam-heated acid waters (e.g. the Lassen volcanic hydrothermal system, USA) are also linked to a lateral outflow where the neutral chloride waters emerge far down-gradient to acid springs.

In contrast, highly-fractured Lava Creek Tuff at Yellowstone, formed around 640,000 years ago, can not serve as a perfect separator for neutral and acid waters. After formed through near-surface oxidation and condensation, acid waters above Lava Creek Tuff, e.g. those from Norris Geyser Basin, were inevitably mixed with deeper neutral chloride-rich waters to generate mixed waters. Since the amount of acid sulfate waters produced in the steam-heated areas at Yellowstone is smaller as compared to that of neutral chloride waters (Allen and Day, 1935), the mixed waters are generally characterized by much higher pH values and chloride concentrations than “pure” steam-heated waters although they may still be acidic.

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In Tibet, the hydrothermal systems are generally not as hot as Yellowstone because of their deeper magmatic heat source. The mixing of glacial water at shallow levels should be common for Tibetan hydrothermal systems and therefore another important reason why they are not hot enough. At least it can be safely concluded that the mixing did occur below the Yangbajain geothermal field as shown in Fig. 7. Thus, there may be less steam created through boiling of deep geothermal fluid in Tibet, which can be demonstrated by taking Yangbajain as an example. As borehole data indicate, the depth of shallow reservoir below Yangbajain is over a range of 180 to 280 m, and the measured temperatures are from 130 °C to 173 °C (Guo et al., 2007). According to the curve of theoretical boiling-point versus depth at various hydrostatic conditions, boiling can not occur at the shallow reservoir of the Yangbajain hydrothermal system.

More importantly, even for those Tibetan geothermal systems where boiling does occur at shallow levels and steam is generated, it seems that there is no a natural means (i.e. a confining layer) to separate the steam and underlying neutral chloride waters like (but not necessary to be) the young impermeable lavas at Yellowstone. In addition to a lateral outflow system based on a confining layer, the steam-heated acid springs can also be formed when the neutral geothermal fluids rise up along an inclined fault, allowing vapors and gases to take a vertical path (fault) to the surface (e.g. the Shoshone Geyser Basin of Yellowstone). For the Tibetan hydrothermal systems, however, the deep neutral brine may ascend along near-vertical faults instead, as we have concluded during our investigation in the Yangbajain geothermal field (Guo et al., 2007). Hence vapor-liquid separation could

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possibly be inhibited at all. Even if it occurred, a backmixing of steam condensates would be inevitable. A case similar to Tibetan hydrothermal systems is the Great Basin in western USA where reservoir temperatures can exceed 200 °C, but faults generally have steep dips and therefore acid sulfate springs formed via steam heating are rare.

Another important factor probably responsible for the lack of steam-heated acid springs in Tibet is that the deep geothermal fluids in Tibetan hydrothermal systems heated by granitic magmas formed via remelting of sedimentary rocks are supposed to carry less H_2S derived directly from magma or from disproportionation of magmatic SO_2 as compared to Yellowstone, Nevado del Ruiz, Miravalles, or other systems whose magmatic heat sources are related to basaltic intrusions. That is, a magma chamber linked to basaltic intrusion can be a potent source of mantle volatiles, including C and S species, which help to promote phase separation and formation of steam-heated acid waters at most magmatic hydrothermal systems on earth. Thus, less acid were generated through oxidation of H_2S in separated geothermal steam for Tibetan systems so that they could be completely neutralized after occurrence of backmixing even if vapor-liquid separation happened. Across Tibet, the concentrations of H_2S and CO_2 in geothermal steam have been measured only at Yangbajain. Nevertheless, a comparison of H_2S and CO_2 percentages in geothermal steam between Yangbajain and Yellowstone (Goff and Janik, 2002; Lowenstern et al., 2012; Zhao et al., 1998a) shows that there are indeed more H_2S and CO_2 in Yellowstone geothermal steams (see Table S3). The abundant H_2S available at the shallow levels below Yellowstone were oxidized to generate numerous acid, steam-heated, sulfate springs there.

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Nevertheless, since detailed geological, geochemical and geophysical studies are absent for most of Tibetan hydrothermal systems as mentioned earlier, the above analyses of factors affecting the possibility for occurrence of steam-heated waters are somewhat speculative. A comprehensive investigation on Tibetan systems, especially in terms of geothermal gas geochemistry, is inevitably needed for fully understanding the geological and geochemical bases for the lack of steam-heated acid waters in Tibet.

5. Conclusions

The possibility for formation of acid, chloride-rich hot springs related to direct uptake of magmatic fluid depends on how deep magma chamber is. The deeper a magmatic heat source is, the more likely the released fluids are neutralized. Among all the hydrothermal systems investigated in this study, Yangbajain, as a representative of Tibetan systems, has the deepest magma chamber (15-18 km), and therefore the Yangbajain geothermal waters, either from hot springs or geothermal wells, are neutral and marked with very low sulfate and magnesium concentrations. In contrast, the lowest degrees of magmatic fluid neutralization occur in Nevado del Ruiz and Miravalles as expected where magmas are very close to the surface, as indicated by the occurrence of strongly acid geothermal springs enriched with both Cl^- and SO_4^{2-}.

The deeper magmatic heat sources below Tibetan systems as well as the mixing of glacial waters also result in that they are usually not as hot as Yellowstone, and consequently less steam is created through boiling of geothermal fluids in Tibet. As compared to Yellowstone, the H_2S concentrations of deep chloride fluids in Tibetan systems

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should be lower as well in view that the basaltic intrusion below Yellowstone serves as a powerful source of mantle S and C species. Thus less sulfuric acid could be produced via oxidation of separated H_2S (if there were any) at shallow levels below Tibetan geothermal areas. Moreover, unlike some hydrothermal areas of Yellowstone where young impermeable lavas can separate H_2S-rich steam from underlying neutral chloride water, there is a lack of such a natural separator in Tibet. Even if vapor-liquid separation occurred, an inevitable backmixing of steam condensates generated within Tibetan systems (usually in very small quantity as discussed) forces them to be fully neutralized by large amounts of underlying neutral chloride fluids.

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Figure captions

Fig. 1. (a) Hydrothermal areas and Late-Cenozoic volcanoes in Tibet. One hundred and ninety-one hydrothermal areas are shown where reliable geothermal water analyses with charge imbalance less than ±15% are available. Four major hydrothermal areas investigated in this study marked with symbols “Yb”, “G”, “Yy” and “L” in the map are Yangbajain, Gudui, Yangyi and Langjiu respectively. Twelve Late-Cenozoic volcanoes shown in the map are: 1, Shenglidaban; 2, Quanshuigou; 3, Liuhuangdaban; 4, Kaerdaxi; 5, Heishibeihu; 6, Dujianshan; 7, Huangyangling; 8, Yongbohu; 9, Bamaoqiongzong; 10, Kushuihuanbei; 11, Heiguoshan; 12, Yuyehu (according to Tong et al. (1990)). (b) Hydrothermal areas in Yellowstone. Only the hydrothermal systems located in the volcanic rock area (marked with ●) are used for comparison with Tibet hydrothermal systems. Those in the sedimentary rock area (marked with ■) are not

considered in this study.

Fig. 2. Plot of pH value vs. SO_4^{2-} concentration for the geothermal waters from Tibet (marked with ○) and Yellowstone (marked with ○). 269 available analyses from 191 Tibet hydrothermal areas and 261 analyses from 17 Yellowstone volcanic-hydrothermal areas (see Fig. 1 for specific locations) with charge imbalance < ±15 % are used for this diagram. Every analysis was obtained from a single geothermal water source (geothermal spring or well). Among 269 analyses of Tibet geothermal water samples, 237 are from Tong et al. (2000), 10 from Japan International Collaboration Agency and Tibet Electric Power Company (2006), 8 from Guo et al. (2009), and 14 are new analyses. All Yellowstone analyses are from USGS Open-File Reports (Ball et al., 2010; Ball et al., 2006; McCleskey et al., 2005; McCleskey et al., 2014).

Fig. 3. Plots of SO_4 vs. Cl (a), Cl vs. pH (b), and SO_4/Cl molar ratio vs. pH (c) for all samples from representative hydrothermal systems. Unless specified otherwise, the legend is the same for the following figures.

Fig. 4. (a) Plot of Na vs. Cl for all samples from representative hydrothermal systems; (b) Plot of K vs. Cl for all samples from representative hydrothermal systems; (c) Plot of Na/Cl milliequivalent ratio vs. (HCO_3+CO_3)/Cl milliequivalent ratio for neutral water samples.

Fig. 5. Plots of Ca vs. Cl (a), Mg vs. Cl (b) and Mg/Cl molar ratio vs. pH (c) for all samples from representative hydrothermal systems. Legend of sample symbols for Fig. 5-c: ○,

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water samples with pHs < 4.5; ●, water samples with pHs > 4.5.

Fig. 6. Variations of pH value as well as sulfate and chloride concentrations of “Crystal Sister East” Spring over time.

Fig. 7. Triangular diagram of Na-K-$Mg^{1/2}$ for water samples.

Fig. 8. Geochemical processes controlling relative Li, Rb and Cs concentrations of geothermal waters.

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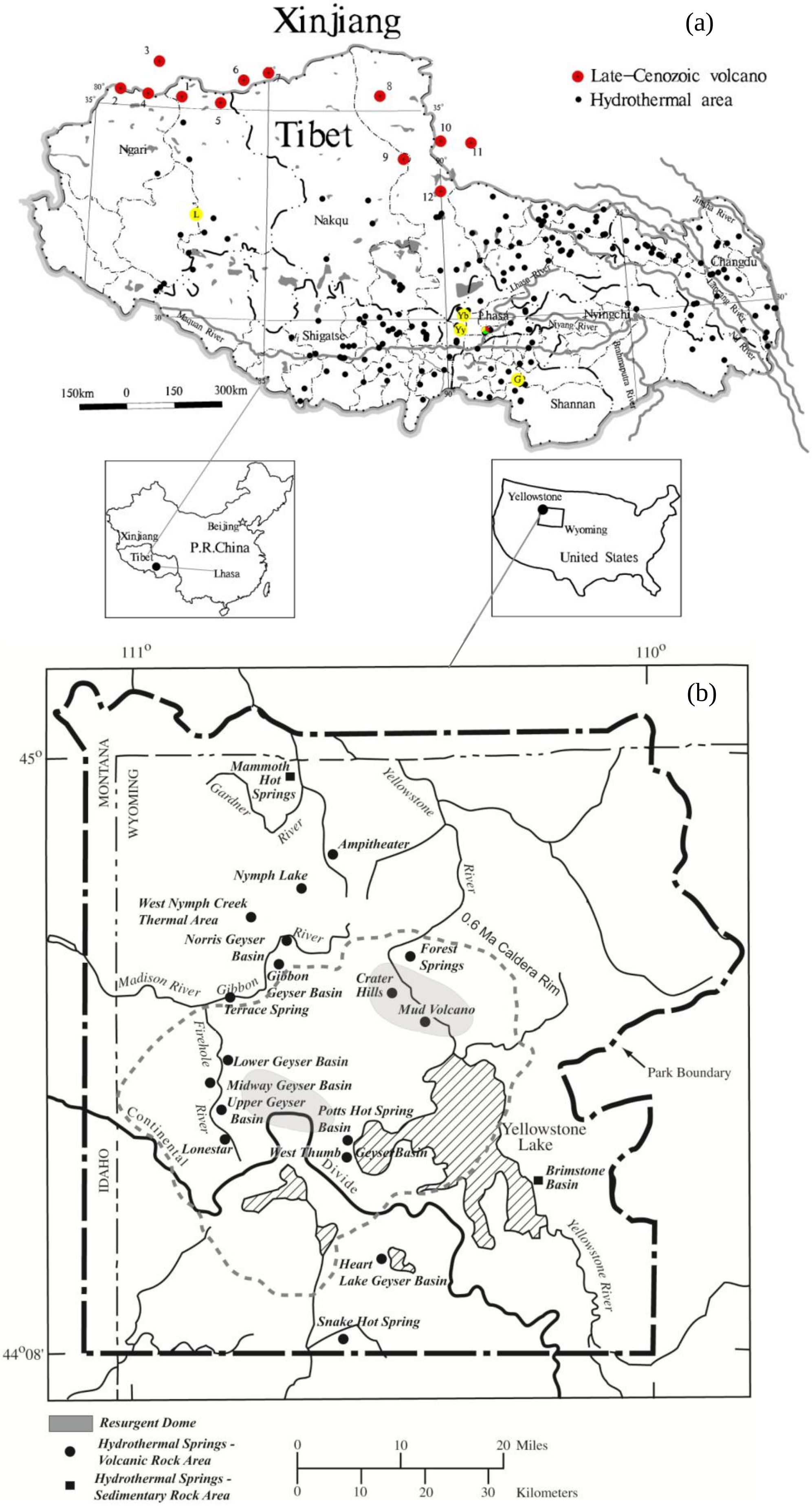

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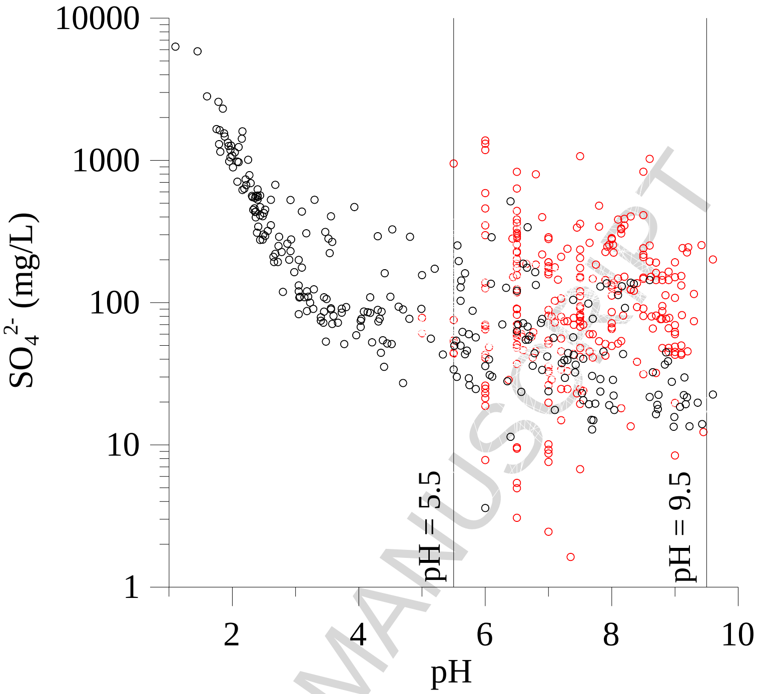

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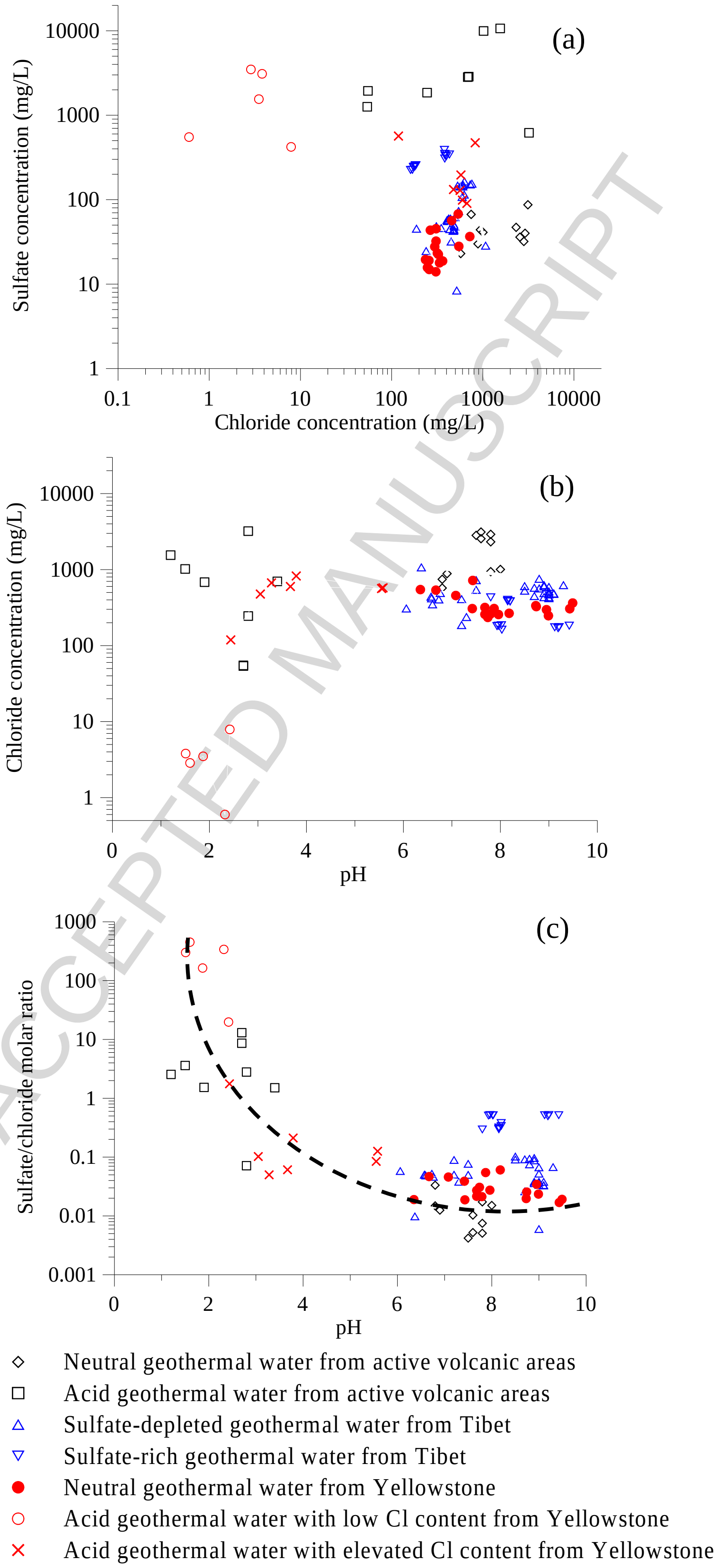

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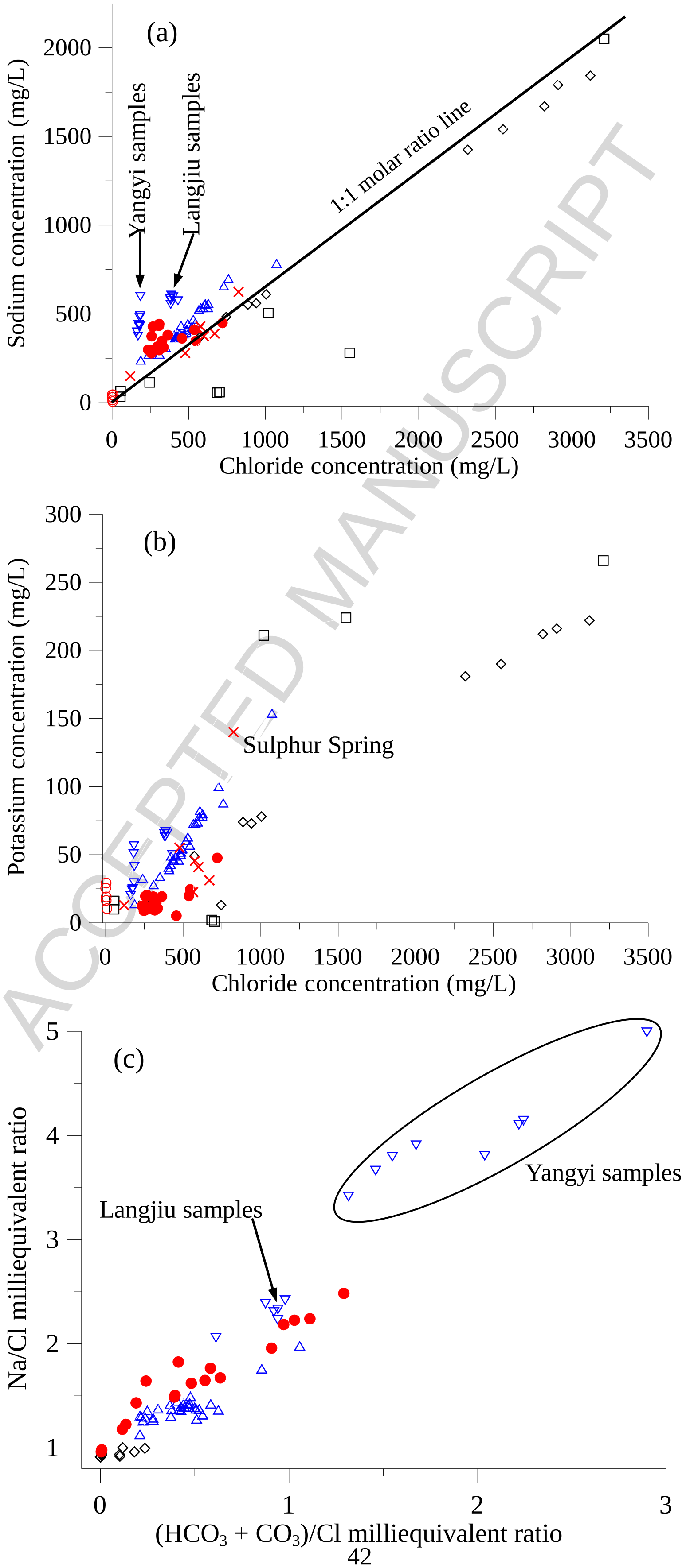

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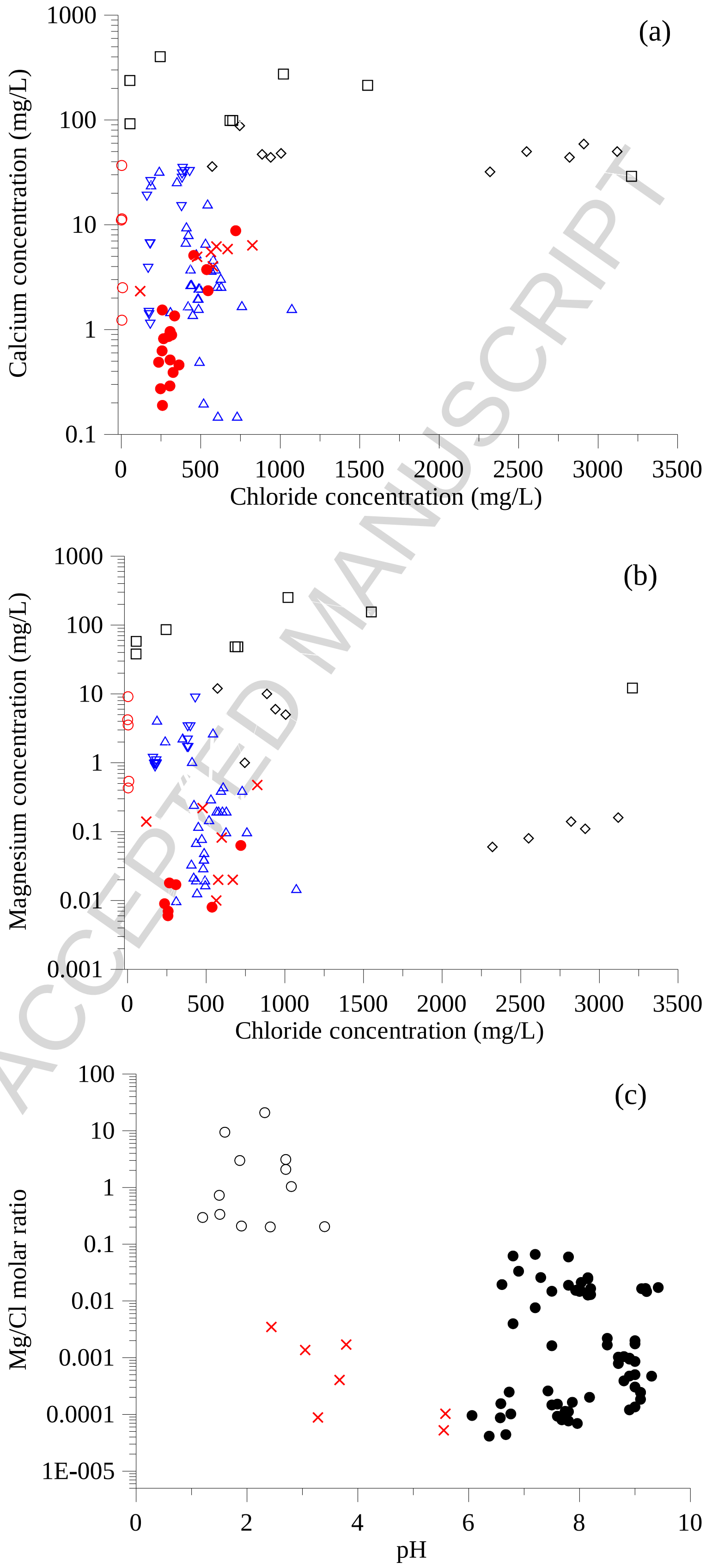

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Fig. 5. Plots of Ca vs. Cl (a), Mg vs. Cl (b) and Mg/Cl molar ratio vs. pH (c) for all samples from representative hydrothermal systems. Legend of sample symbols for Fig. 5-c: ○, water samples with pHs < 4.5; ●, water samples with pHs > 4.5.

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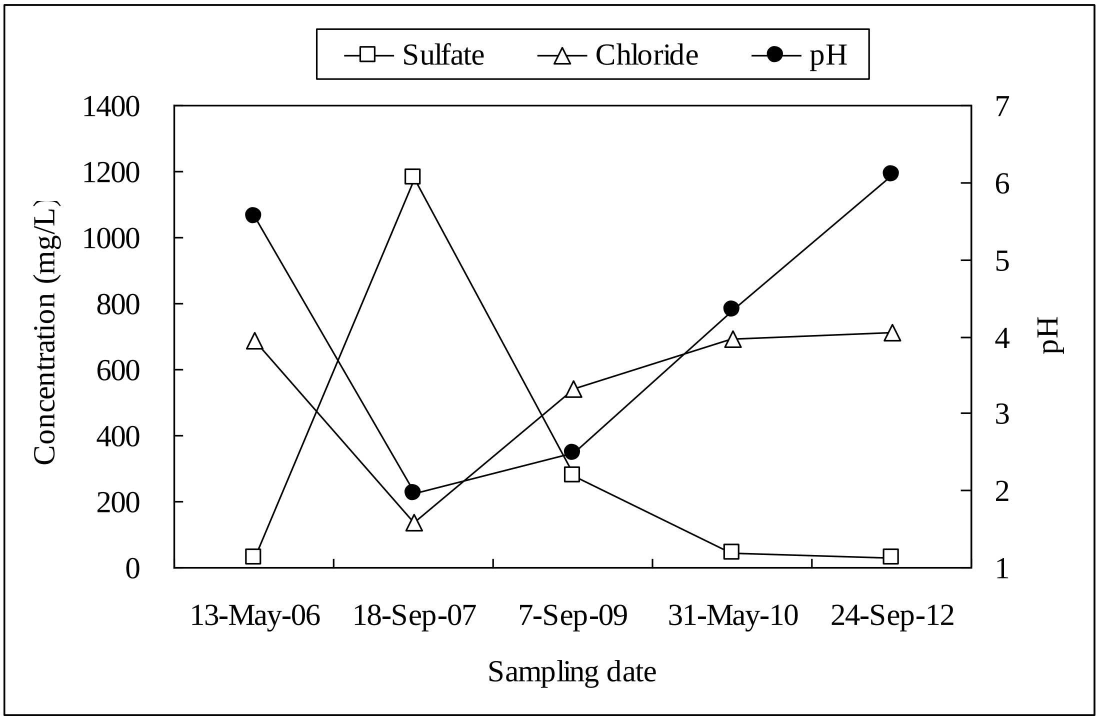

Fig. 6. Variations of pH value as well as sulfate and chloride concentrations of "Crystal Sister East" Spring over time.

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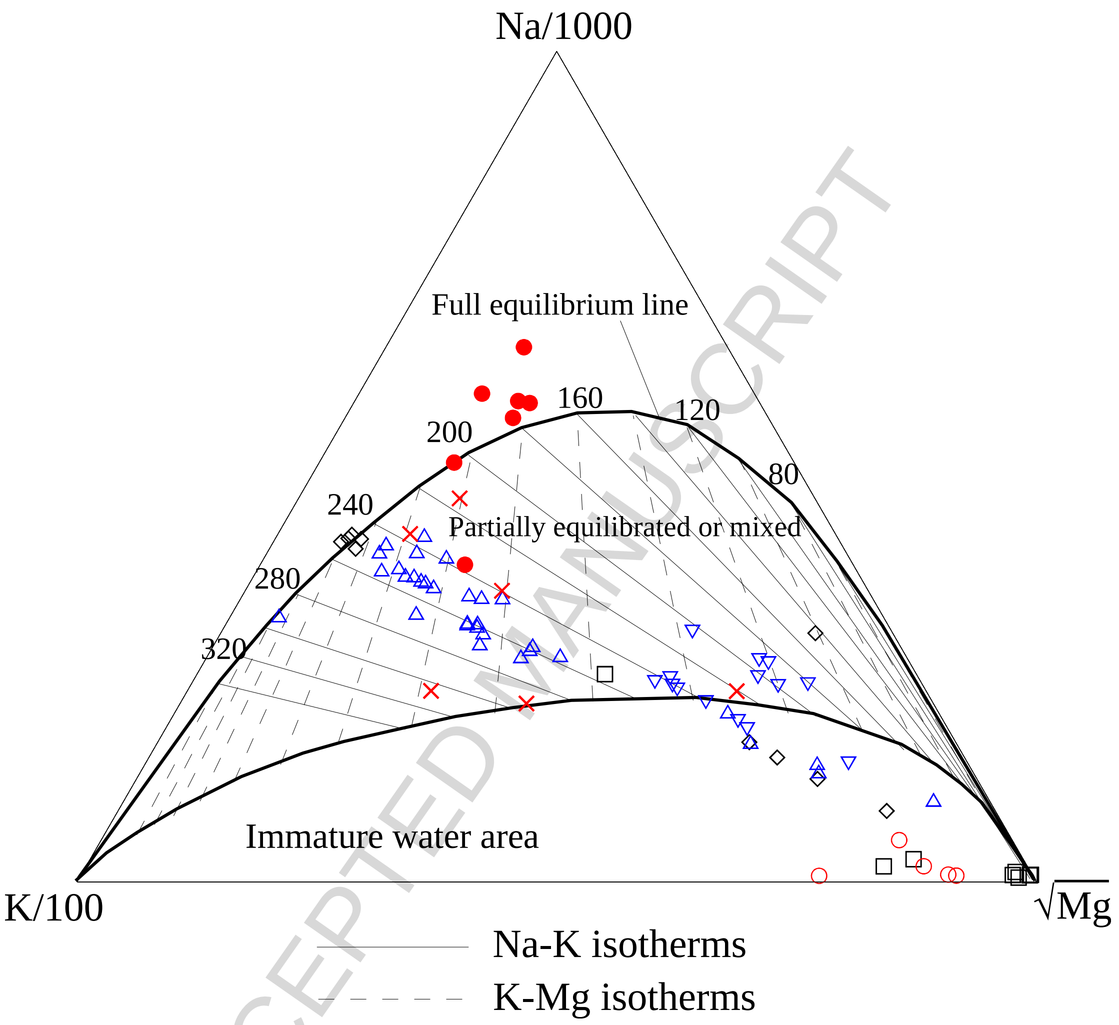

Fig. 7. Triangular diagram of Na-K-$Mg^{1/2}$ for water samples.

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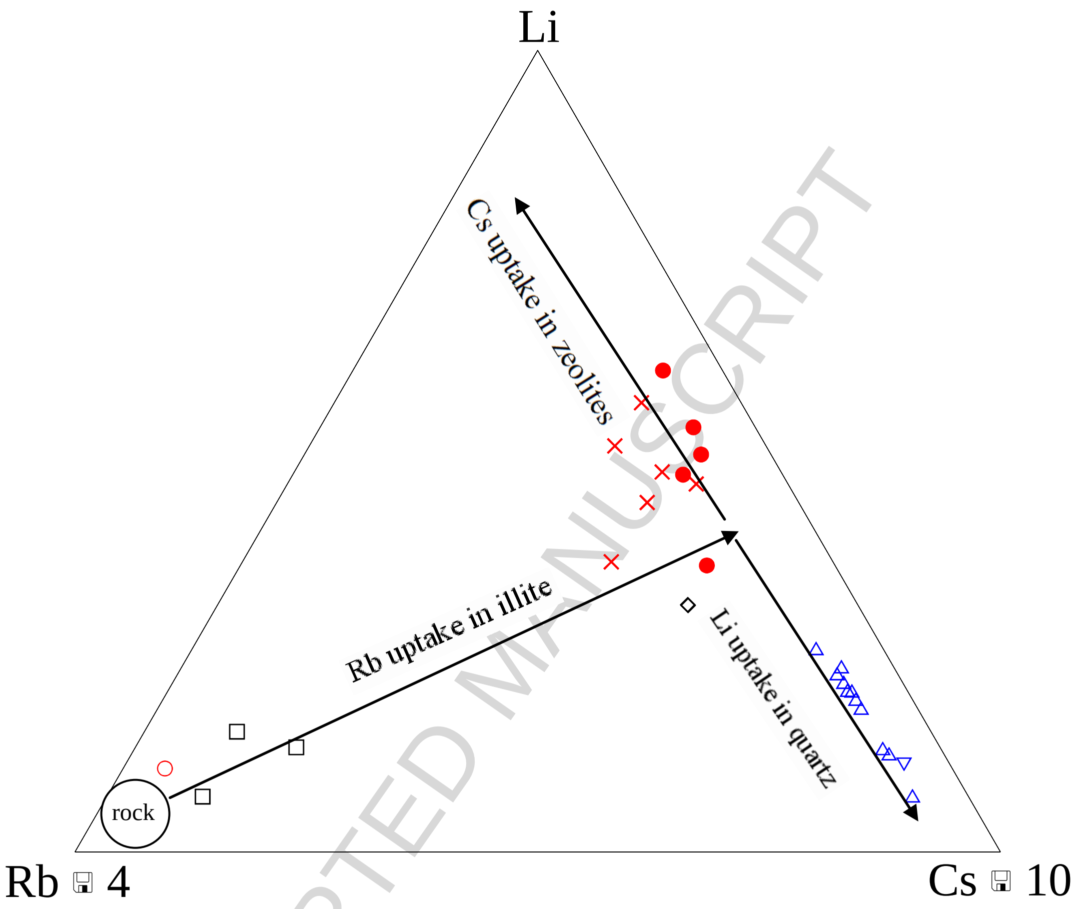

Fig. 8. Geochemical processes controlling relative Li, Rb and Cs concentrations of geothermal waters.

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Table 1. Geographic, geological and geothermal characteristics of the Yangbajain, Gudui, Yangyi, Langjiu and Nakqu geothermal fields.

Geothermal field	*Altitude (m)*	*Average annual air temperature (°C)*	*Reservoir thickness (m)*	*Reservoir lithology*	*Cap rocks*	*Highest measured reservoir temperature (°C)*	*Depth for highest temperature (m)*	*Deepest borehole (m)*	*Major discharge way*
Yangbajain in geothermal field	4300-4500	2.5	About 900	Himalayan granitic mylonite and fractured granite	Intensively eroded Himalayan granite and biotite granite	329.8	1850	1850	Geothermal production wells
Gudui geothermal field	4400-4700	8.2	unknown	unknown	unknown	--	--	--	Natural springs
Yangyi geothermal field	4550-5050	1.1	400-500	Himalayanian biotite granite and biotite granite porphyry	Intensively eroded Miocene volcanic rock	207.2	313	953	Natural springs and abandoned geothermal wells
Langjiu geothermal field	～4500	0.2	unknown	Late-Cretaceous fractured granite	non-existent	105.0	～100	～100	Natural springs and abandoned geothermal wells
Nakqu geothermal field	4480-4520	-1.9	> 700	Jurassic sandstone	Silicified sandstone	116.0	693	708	Natural springs and abandoned geother

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Table 2. Analytical techniques used for measurements of major cations (Na, K, Ca, Mg, Li, Rb and Cs), anions (SO_4^{2-}, Cl^-, F^- and Br^-) and other constituents (As, B, SiO_2, Al, Fe, H_2S and NH_4^+) in geothermal water. n.a.: not analyzed.

Sampling site	***Collected by***	***Data source***	***Analytical methods***					
			Na	**K**	**Ca**	**Mg**	**Li**	**Rb**
Tibet	Tong et al.	Tong et al. (2000)	F-AES	F-AES	EDTA titration	EDTA titration	AAS	AAS
	JICA and TEPC	JICA and TEPC (2006)	F-AES	F-AES	ICP-AES	ICP-AES	ICP-AES	n.a.
	Authors of this paper	Guo et al. (2009)	IC	IC	IC	IC	ICP-MS	n.a.
	Authors of this paper	New analysis	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-MS	n.a.
Yellowstone	Authors of this paper	McCleskey et al. (2005, 2014), Ball et al. (2006, 2010)	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES; ICP-MS	ICP-AES; ICP-MS

Sampling site	***Collected by***	***Data source***	***Analytical methods***					
			Cs	SO_4^{2-}	Cl^-	F^-	Br^-	***As***
Tibet	Tong et al.	Tong et al. (2000)	AAS	Turbidimetry	Titration	Colorimetry	n.a.	Colorimetry
	JICA and TEPC	JICA and TEPC (2006)	n.a.	IC	IC	IC	IC	ICP-AES
	Authors of this paper	Guo et al. (2009)	n.a.	IC	IC	IC	n.a.	ICP-MS
	Authors of this paper	New analysis	n.a.	IC	IC	IC	IC	ICP-MS
Yellowstone	Authors of this	McCleskey et al.	ICP-MS	IC	IC	ISE; IC	IC	ICP-AES; HGAAS

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	paper	(2005, 2014), Ball et al. (2006, 2010)

Sampling site	***Collected by***	***Data source***	***Analytical methods***					
			B	***SiO_2***	***Al***	***Fe***	***H_2S***	***NH_4^+***
Tibet	Tong et al.	Tong et al. (2000)	Colorimetry	Colorimetry	n.a.	n.a.	Iodimetric titration	Colorimetry
	JICA and TEPC	JICA and TEPC (2006)	ICP-AES	Gravimetric	ICP-AES	ICP-AES	Iodimetric titration	n.a.
	Authors of this paper	Guo et al. (2009)	ICP-MS	Colorimetry	ICP-MS	ICP-MS	n.a.	n.a.
	Authors of this paper	New analysis	ICP-MS	ICP-AES	ICP-MS	ICP-MS	n.a.	n.a.
Yellowstone	Authors of this paper	McCleskey et al. (2005, 2014), Ball et al. (2006, 2010)	ICP-AES; ICP-MS	ICP-AES	ICP-AES; GFAAS	ICP-AES; Colorimetry	Colorimetry; ISE	Colorimetry; IC

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Highlights

- Acid geothermal springs don’t exist in Tibet
- Formation of acid springs via direct uptake of magmatic fluid depends on depth of magma chamber
- Multiple factors are responsible for the lack of steam-heated acid waters in Tibet

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