Journal of Geochemical Exploration 148 (2015) 96–104

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Geochemistry and fluoride levels of geothermal springs in Namibia

O. Sracek [a,*], H. Wanke [b], N.N. Ndakunda [b], M. Mihaljevič [c], F. Buzek [d]

[a] Department of Geology, Faculty of Science, Palacky University, Olomouc, Czech Republic
[b] Department of Geology, University of Namibia, Windhoek, Namibia
[c] Department of Geochemistry, Mineralogy, and Natural Resources, Faculty of Science, Charles University, Praha, Czech Republic
[d] Czech Geological Survey, Praha, Czech Republic

ARTICLE INFO

Article history:
Received 20 April 2014
Accepted 26 August 2014
Available online 16 September 2014

Keywords:
Namibia
Geothermal springs
Fluoride
Stable isotopes

ABSTRACT

A survey of groundwater from six geothermal springs in Namibia showed high concentrations of dissolved fluoride, with values up to 18.9 mg/l. All values are higher than both the WHO limit and the Namibian guideline. High concentrations of fluoride are linked to Na-HCO_3 or Na-SO_4-HCO_3 groundwater types, with increasing sulfate and chloride concentrations towards the south of Namibia. Values of δ^2H and $\delta^{18}O$ are more negative for the north of the country, and with increasing altitude of springs and distance from precipitation sources towards the southeast from the Indian Ocean. A shift of about 1‰ from the LMWL for Windhoek was observed for $\delta^{18}O$ samples, which was probably caused by the exchange with reservoir rocks. Values of $\delta^{34}S(SO_4)$ reflect mixing of two principal sulfate sources, i.e., dissolution of gypsum originating from playas and interaction with sulfidic mineralization in tectonic bedrock zones. Values of $\delta^{13}C$(DIC) seem to be affected by a variable vegetation cover and mainly by the input of endogenous CO_2. Estimated reservoir temperatures vary from 60 °C to 126 °C, with a maximum value at the Ganigobes site. The geothermal springs of Namibia in this study do not meet drinking water standards and thus their water can be used only for other purposes e.g. for thermal spas. Treatment would be necessary to decrease dissolved fluorine concentrations for drinking water purposes.

1. Introduction

Namibia is a country in southwestern Africa experiencing from semiarid to extremely arid climate. This is a consequence of the cold Benguela Current flowing west of the Namibian coast. Water resources here are very scarce and water supply is of a serious concern. In coastal zone harvesting of water condensed from fog is a standard practice (Shanyengana et al., 2002). Thermal waters in Namibia have been known as early as 1837 at the capital Windhoek, locally known by the Nama people as Ai=//gams (fire water) and by the Herero people as Otjomuise (the place of smoke). Geothermal waters discharge in several springs in Namibia, usually located on tectonic lines. Locations of the springs included in this study are given in Fig. 1a. High concentrations of fluoride may represent a problem for exploitation of geothermal waters in the country.

Fluorine occurrence is widespread in the lithosphere as a component of rocks and minerals. The earth's crust contains abundant fluorine in calcium granite (520 ppm), low calcium granite (850 ppm), alkaline rocks (1200–8500 ppm), shale's (740 ppm), sandstone (270 ppm), deep sea clay (1300 ppm), and in deep sea carbonates (540 ppm) (NEERI, 1985). Fluorine is sparingly soluble in water, hence due to its highly electronegative characteristics it forms only fluorides and no other oxidation states are found in natural water (Hem, 1992). Fluorite (CaF_2) is the principal rock-forming mineral that has fluorine as an essential constituent and has generally been considered as a dominant source of groundwater fluorine, especially in granitic terrain. Fluoride concentration in groundwater is frequently proportional to the degree of water–rock interaction because fluoride primarily originates from geological sources (Banks et al., 1995; Carillo-Rivera et al., 2002; Gizaw, 1996). The potential geogenic sources of fluoride in groundwater include various soils and minerals in rocks, such as topaz, fluorite, fluorapatite, cryolite, amphiboles, and micas (Bardsen et al., 1996; Handa, 1975; Pickering, 1985; Subba Rao and Devadas, 2003; Wenzel and Blum, 1992).

Apatite is present in sedimentary rock and fluorite often occurs as a cementing material in sediments. A positive correlation between fluoride and dissolved silica as well as between fluoride and sodium also supports the silicate origin of fluoride (Chae et al., 2006; Koritnig, 1992). However, quantitative assessments of fluoride enrichment in natural waters, especially through the study of fluid–mineral equilibria, are sparse (Saxena and Ahme, 2001).

Fluoride belongs to a family of so-called geogenic contaminants: its enrichment in water is not generally a consequence of human activities (Johnson et al., 2011), but rather natural processes. It is a serious problem in many countries including Ethiopia (Tekle-Haimanot et al., 2006), Kenya (Gaciri and Davies, 1993), India (Jacks et al., 2005), Sri Lanka (Dissanayake and Chandrajith, 2007), Mexico (Armienta and Segovia,

* Corresponding author. Tel.: +420 585634537; fax: +420 585225737.
E-mail address: srondra@yahoo.com (O. Sracek).

http://dx.doi.org/10.1016/j.gexplo.2014.08.012
0375-6742/

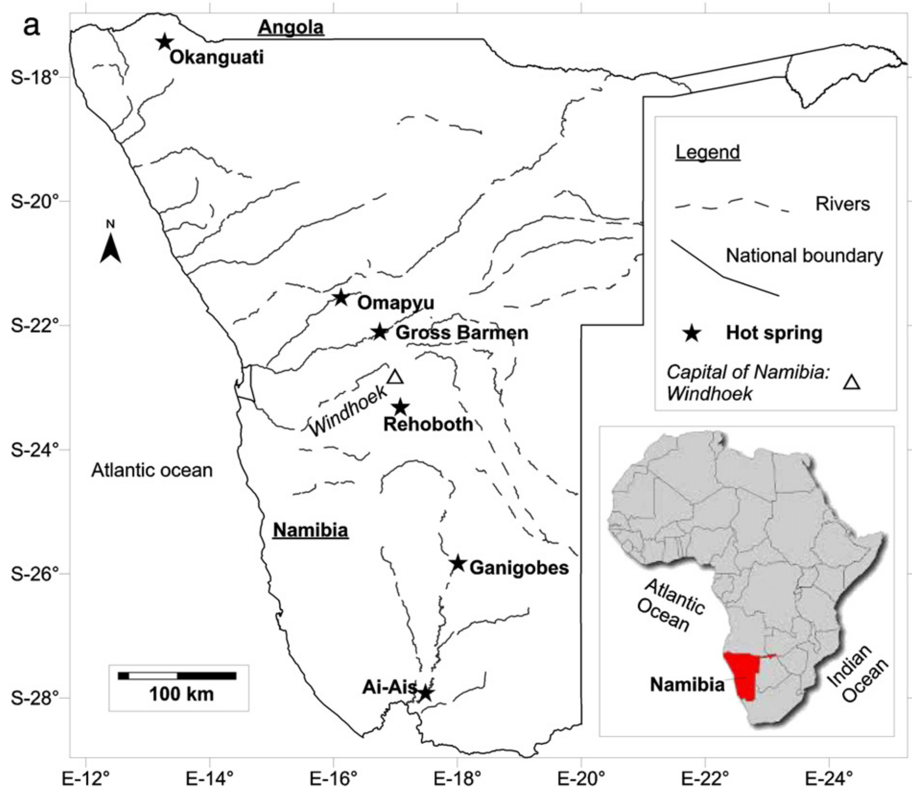

Fig. 1. (a) Location of sampled geothermal springs in Namibia, (b) geological map of Namibia. (adapted from Petzel and Schreiber, 1999)

2008), and Argentina (Bhattacharya et al., 2006). Its high concentrations are generally linked to high residual alkalinity ($Ca^{2+} < HCO_3^-$), high Na^+, and high pH waters (Jacks et al., 2005; Sracek and Hirata, 2002). In high Ca^{2+} waters fluoride precipitates as fluorite (CaF_2) which generally controls maximum fluoride concentration in waters.

The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization, (WHO, 1998), is 1.5 mg/l. However, fluorine is also essential for human beings as it helps in normal mineralization of bones and formation of dental enamel. It adversely affects human health when its concentration exceeds the limit of 1.5 mg/l. In some countries, fluorine is added to water in small amounts to prevent health hazards. However, ingestion of water with fluoride concentrations above 1.5 mg/l results in dental fluorosis characterized initially by opaque white patches, staining, mottling, and pitting of teeth (Kundu et al., 2001). In an advanced stage, deformation of bones occurs because fluorine in human body interferes with the metabolism of calcium (Rango et al., 2012).

Skeletal fluorosis may occur when fluoride concentrations in drinking water exceed 4–8 mg/l, which leads to an increase in bone density, calcification of ligaments, rheumatic or arthritic pain in joints and muscles along with stiffness and rigidity of the joints, bending of the vertebral column, and so on. Fluoride has the same effect on livestock as in humans, with concentrations above 2 mg/l affecting animal breeding and causing mottled teeth in young animals. The bone joints of some animals may become swollen and painful resulting in shifting lameness, stiffness of joints and backbones (Sudarshan and Rajeswara Reddy, 1991). High concentration of fluoride in irrigation water prevents the accumulation of chlorophyll in plant leaves.

Other geothermal species of concern in the Namibian springs are boron, uranium and especially arsenic. In geothermal reservoirs, arsenic is generally present in Na-Cl type of water in acid igneous rocks (Birkle et al., 2010; López et al., 2012; Webster and Nordstrom, 2003).

The main objective of the study was to explain the geochemical and isotopic composition of the geothermal waters in Namibia including levels and behavior of fluoride.

2. General geology and description of spring sites

In Namibia a total of 24 springs are reported as thermal, of which nine are scalding (Kent, 1949). Six out of these springs were sampled for this study: the springs in Rehoboth, Gross Barmen, Ganigobes, Omapyu, Okanguati, and Ai-Ais (Fig. 1a). Several other springs could not be sampled as groundwater levels had dropped and springs stopped discharging (e.g. springs in Windhoek).

Geological map of the study area is shown in Fig. 1b. Most hot springs in Namibia are situated within areas dominated by the Damara Orogenic belt which forms a part of the Pan-African tectono-thermal belts that surround and dissect Africa. The Damara Orogen occurred during the Neoproterozoic and early Paleozoic between 750 and 450 Ma ago (Schneider, 2008). According to Miller (2008), the Damara Belt consists of the NNW trending coastal arm, the Kaoko Belt which extends into Angola and continues northward and has a NE trending arm, and the Damara Belt, which extends through central Namibia across northern Botswana to the Zambezi Belt and the Mozambique Belt.

The Damara Belt was formed during the collision between the Congo Craton in the north and the Kalahari Craton in the south. During the collision, the Kalahari Craton was subducted underneath the Congo Craton, and it was accompanied by major deformation, metamorphic and intrusion events.

The Damara Belt shows well-preserved bivergent symmetry typical for collisional belts. Based on lithological, structural and metamorphic characteristics, the Damara Belt is subdivided into contrasting tectonostratigraphic zones from the north to the south, into the Northern Platform, Northern Marginal Zone, Northern Zone, Central Zone,