Large Si isotope fractionation reveals formation mechanism of quartz in silicon-poor carbonatite

Yong-Shu Huang[1,2], Qi Liu[3], Fei-Xiang Liu[3], Xiao-Chun Li[2,4], Yu Liu[1], Guo-Qiang Tang[1], Hong-Rui Fan[2,4], Xian-Hua Li[1,2], and Qiu-Li Li[1,2,*]

[1]State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
[2]College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
[3]State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China
[4]Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

ABSTRACT

Carbonatites, the most silica-poor igneous rocks, have a close relationship with rare earth element (REE) ore deposits, where low SiO_2 activity is considered to contribute to economic REE mineralization. However, a paradox is raised by quartz, commonly regarded as a Si-saturation proxy, which occurs in some giant carbonatites or carbonatite-related REE deposits such as those at Bayan Obo, China, and Mountain Pass, California, USA. A unique perception for the origin of quartz in carbonatites is provided here using Si isotope analysis. Quartz grains from the Bayan Obo carbonatite and REE ores commonly occur as inclusions in fluorite, or they coexist with fluorite, thus implicating the importance of fluorine in their hydrothermal origin. The quartz grains have remarkably large variations in $\delta^{30}Si$ values, ranging from $-4.55‰$ to $1.71‰$ in secondary ion mass spectrometry analyses, which have not been documented elsewhere in high- to medium-temperature magmatic-hydrothermal processes. Theoretical calculations demonstrate that such large Si isotopic fractionation can be generated during the formation and breakdown of Si-O and Si-F bonds due to their difference in bond strength. These results imply the presence of silicon fluoride species in the fluid and highlight the role of fluorine in quartz formation in silicon-poor carbonatite. The exsolved fluids from carbonatite magmas containing silicon fluoride species may decrease silica activity, which has the potential to impede incorporation of REEs into magmatic apatite, and thus facilitate late-stage hydrothermal REE enrichment and formation of REE orebodies.

INTRODUCTION

Rare earth elements (REEs) are widely utilized for their excellent optical and magnetic properties, and they are critical metals for the establishment of green energy systems. REEs are rare components in Earth's crust, and hence REE deposits are restricted to a few specific geological settings, in which carbonatite-type REE ores are most common and are the major source of REEs worldwide (Weng et al., 2015).

Carbonatites are recognized as the globally most silica-poor igneous rocks, with SiO_2 generally <20 wt% (Massuyeau et al., 2015). Due to low silica activity, silicate minerals like quartz, feldspars, and orthopyroxene are unlikely to

Qiuli Li https://orcid.org/0000-0002-7280-5508
*liqiuli@mail.iggcas.ac.cn

be stabilized as primary magmatic phases in carbonatites (Barker, 2001). Low SiO_2 activity is also considered to impede both the ability of apatite to capture REEs in carbonatite and to facilitate the enrichment of REEs in fluids (Anenburg et al., 2020). However, quartz has been recorded from numerous carbonatites and coexists with hydrothermal minerals such as fluorite, bastnäsite, and barite in some carbonatite-type REE deposits, including those at Bayan Obo in China, Mountain Pass in North America, and Amba Dongar in India (Doroshkevich et al., 2009; Verplanck et al., 2014; Liu et al., 2018b). Different researchers have proposed that quartz originates from the fractional crystallization of parental carbonatite magma or by contamination related to assimilation of wall rocks during the ascent of magma (Doroshkevich et al., 2009).

Another hypothesis is that the quartz in REE ores may originate from xenocrysts or external silica-rich fluids (Chebotarev et al., 2018; Liu et al., 2018a; Giebel et al., 2019; Anenburg et al., 2020). Thus, the mechanism for the formation of quartz in low-silica-activity, carbonatite-type REE deposits is still debated.

This study elucidated the fluid reactions that control the formation of quartz in carbonatites using Si isotope analyses and theoretical calculations, with a particular emphasis on the role of fluorine in the hydrothermal fluids associated with carbonatitic systems, using Bayan Obo as a key example.

GEOLOGICAL SETTING AND SAMPLE SELECTION

The Bayan Obo REE-Nb-Fe deposit is located on the northern margin of the North China craton (Fig. 1). The country rocks to orebodies are a suite of low-grade metasedimentary rocks of the Mesoproterozoic Bayan Obo Group, including nine units (H1–H9) within the sedimentary sequence (Chao et al., 1997). All REE-Nb-Fe orebodies (main, east, and west) are hosted within silica-poor dolomite previously classified as unit H8, which is overlain by a suite of slate and schist, classified as unit H9, in the Bayan Obo Group (Fig. 1). Permian granite that is exposed around the mine area is intruded into the mineralized dolomite in places. Rather than a sedimentary unit, the ore-hosting dolomite is shown to be a complex carbonatite intrusion emplaced into units H7 and H9 in the Bayan Obo Group, and its mantle-like Sr and Nd isotope values are consistent with this interpretation (Yang et al., 2019). In this study, seven representative REE ore samples were collected, comprising a fluorite-bearing host dolomite and six banded ore samples (Figs. 2A, 2D,
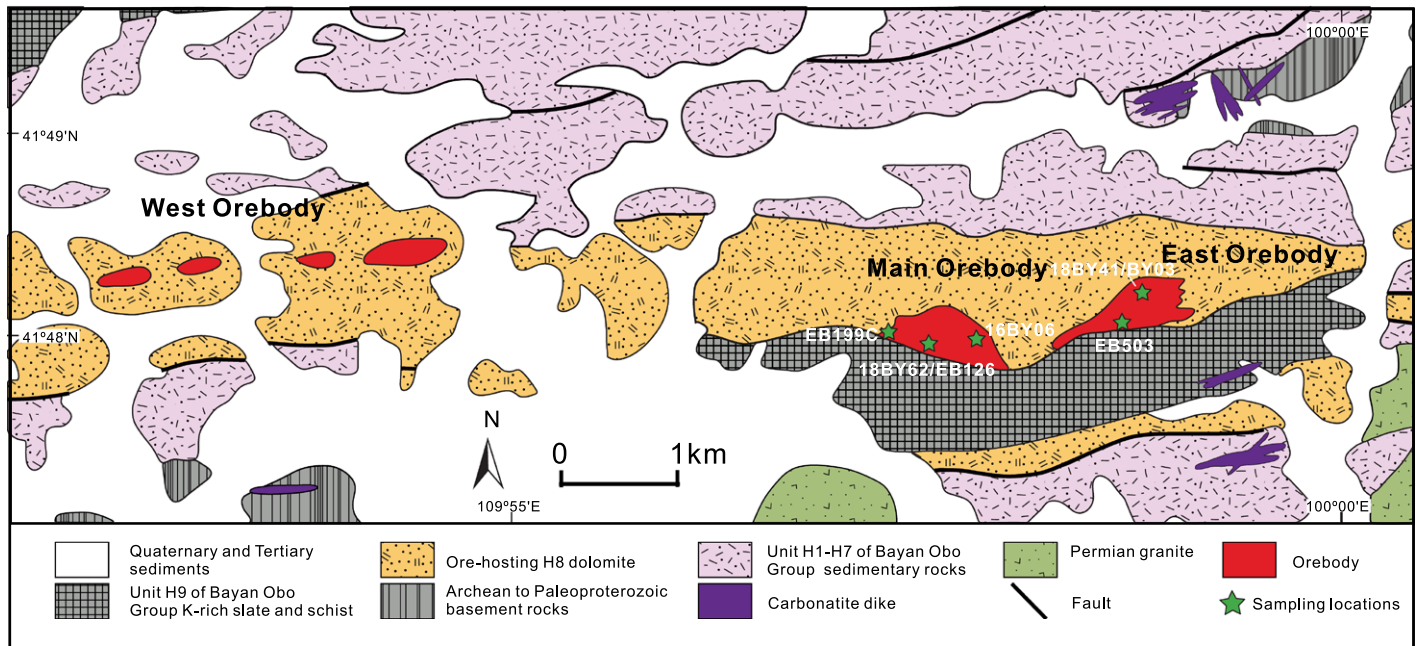
Figure 1. Geological map of Bayan Obo rare earth element deposits with sampling locations (green stars) (modified after Yang et al., 2019).

and 2G), together with a K-rich slate from the H9 unit and a quartz vein that crosscuts the REE ores.

Optical microscope and scanning electron microscope (SEM) images revealed that quartz is widespread in dolomite and is associated with fluorite (Figs. S1A and S1B in the Supplemental Material[1]). In all six banded ores, quartz has a wide distribution in layers of monazite-bastnäsite-magnetite-fluorite-barite-apatite (Figs. 2B, 2E, and 2H; Figs. S1C, S1D, S2, and S3). Unzoned quartz grains (cathodoluminescence [CL] images: Figs. 2C, 2F, and 2I) are mainly enclosed in or coexist with fluorite, with a few grains coexisting with REE minerals (mostly bastnäsite, monazite), barite, magnetite, and apatite (Figs. 2B, 2E, and 2H; Figs. S1, S2, and S3). Inclusions of hydrothermal minerals such as fluorite, magnetite, monazite, and bastnäsite in quartz grains (Figs. 2C and 2E) are common.

RESULTS

In situ quartz Si isotope analyses were conducted using secondary ion mass spectrometry (SIMS) with a CAMECA IMS 1280. Detailed analytical procedures are described in Supplemental Note 1. Among the six banded ores, quartz grains were generally depleted in ^{30}Si with a range of $\delta^{30}Si$ from $-4.55‰$ to $1.71‰$, and an average value of $-1.19‰$. The variation range of $\delta^{30}Si$ values at single thin-section scale reached up to $4.2‰$. The $\delta^{30}Si$ value of quartz in dolomite ranged from

$-2.03‰$ to $1.31‰$ at the thin-section scale, with an average value of $-0.08‰$ (Fig. 3; see Table S2; Fig. S4). The Si isotope variation of single-grain quartz varied from to $-2.49‰$ to $-0.40‰$ in sample 16BY06 (Fig. 2E). Quartz from K-rich slate and quartz veins that crosscut the REE ores gave similar values of $-0.03‰ \pm 0.30‰$ (2 standard deviation [2SD]) and $-0.09‰ \pm 0.15‰$ (2SD), respectively (Fig. 3; Table S3), which falls within the variation range of sedimentary rocks ($-0.82‰$ to $0.01‰$; Savage et al., 2013).

DISCUSSION

Formation Mechanism of Quartz in Carbonatite

Carbonatites are igneous rocks with high carbonate mineral content (>50 wt%) and low SiO_2 content (<20 wt%) (Le Maitre et al., 2002). Bayan Obo REE ores have an average SiO_2 content of $\sim10\%$ (Hao et al., 2010). There are three potential genetic models for generation of disseminated quartz in such silicon-poor carbonatite systems: (1) fractional crystallization from the carbonatite magma; (2) preservation of residue minerals from country rock; or (3) deposition from REE ore-forming fluid.

In terms of the first model, silica activity is generally low in carbonatite magmas. Due to the extremely low Si partition coefficient between carbonatitic primary carbonatite minerals and melts, the crystallization of quartz may occur during fractional crystallization in specific and local environments (Williams-Jones and Palmer, 2002; Doroshkevich et al., 2009). If quartz simply crystallizes from carbonatite magma, its $\delta^{30}Si$ value should fall within the range of igneous rock silicon isotopes ($-0.40‰$

to $\sim-0.10‰$; Poitrasson, 2017). However, such a data range is not recorded.

The second model suggests that the quartz in carbonatite comes from the residue of country rock (Liu et al., 2018a; Anenburg et al., 2021). Banded iron formations (BIFs) and cherts are the only terrestrial samples with a comparable $\delta^{30}Si$ range ($-3.7‰$ to $5‰$) in major reservoirs (Poitrasson, 2017). The large variation in Si isotope compositions of quartz in REE ores and carbonatite could potentially be attributed to residue of quartz from these rock types. However, BIFs and cherts are absent in the country rock sequences that enclose the Bayan Obo deposit. In addition, this model cannot explain the inclusions of REE minerals in quartz.

In terms of the third model, petrographic relationships, including the coexistence of quartz with fluorite, and the inclusion of magnetite, apatite, and REE minerals in quartz (Fig. 2) indicate that quartz was precipitated from fluorine-rich fluids containing REEs.

Fluorine Effect on Quartz Precipitation

As noted above, the third hypothesis—that the quartz grains are the products of fluorine-rich fluid activity—is supported by petrographic evidence, but the role of fluorine in quartz precipitation has received little attention. Mitra and Rimstidt (2009) reported that SiF_6^{2-} is an important ligand to enhance the transport and solubility of Si, and large quantities of volatile SiF_4 have been detected during the degassing of volcanoes (Mori et al., 2002). Therefore, a possible role of fluoride is to enhance the solubility of silica, and there are two potential sources of silica: (1) carbonatite magma and (2) country rocks.
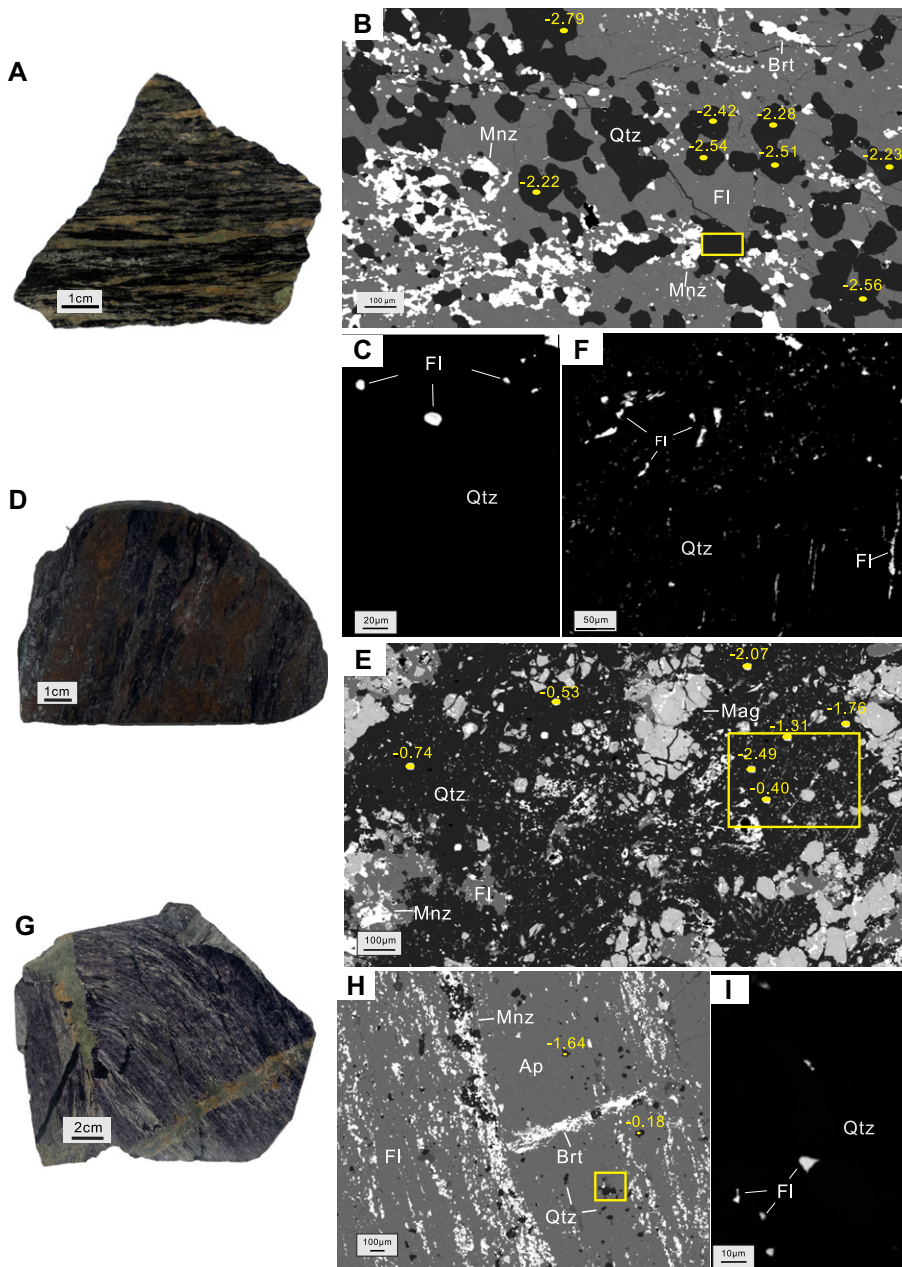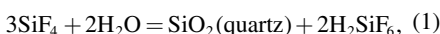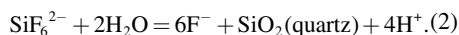
Figure 2. (A, D, G) Polished slabs, (B, E, H) backscattered-electron (BSE) images, and (C, F, I) cathodoluminescence (CL) images of some typical banded rare earth element (REE) ore samples in Bayan Obo: BY03 (A, B, C), 16BY06 (D, E, F), and EB199C (G, H, I). Hydrothermal minerals, mainly made up of fluorite, magnetite, bastnäsite, monazite, barite, apatite, and quartz, are dispersed in banded mineral aggregates. Most of quartz is included in fluorite. Hydrothermal inclusions of fluorite, magnetite, bastnäsite, and monazite are present in some quartz grains. Yellow boxes (B, E, H) show quartz grains that were selected for CL images (C, F, I). Yellow dots (B, E, H) are positions of SIMS Si isotope analyses, with δ^{30}Si values labeled. Ap—apatite; Brt—barite; Fl—fluorite; Mag—magnetite; Mnz—monazite; Qtz—quartz.

$$3Ca(Mg, Fe)(CO_3)_2(dolomite) + 8H^+$$
$$+ SiF_6^{2-} = 3(Mg,Fe)^{2+} + 3CaF_2(fluorite)$$
$$+ SiO_2(quartz) + 6CO_2 + 4H_2O. \quad (3)$$

This reaction can explain why quartz and fluorite commonly occur together in REE ores. The petrographic evidence from sample 18BY41 (Figs. S1A and S1B) supports Equation 3, which involves only dolomite, fluorite, and bastnäsite. Moreover, the reaction between fluoride-rich fluids and carbonatite would produce a large amount of CO_2, and a study of fluid inclusions in main-stage banded ores reported high CO_2 contents with $X_{(CO2)}$ values ranging from 0.1 to 0.3 at temperatures of ~300 to >400 °C and pressures of >0.9–1.4 kbar (Smith and Henderson, 2000). The solubility of quartz is especially sensitive to the CO_2 content. The addition of CO_2 could result in the fluid becoming oversaturated with quartz (Newton and Manning, 2000).

It is also notable that emplacement of fluid-rich carbonatite magmas is commonly accompanied by large-scale fenitization, which is traditionally believed to involve the removal of silica from country rocks into the fluids (Elliott et al., 2018). The fluids that induce fenitization are commonly rich in halides, principally fluorine (Le Bas, 2008). These reactions can be expressed as follows:

$$4H^+ + 4F^- + silicate\ minerals = SiF_4 + 2H_2O + OCSM, \quad (4)$$

and

$$4H^+ + 6F^- + silicate\ minerals = SiF_6^{2-} + 2H_2O + OCSM, \quad (5)$$

where OCSM stands for other components of silicate minerals.

Acidic volcanic rocks can be metasomatized by F-rich hydrothermal fluids to form distinctive zones with irregular and amoeboid shapes (McPhie et al., 2011). Hydrofluoric acid is the major dissolving agent for silicate minerals in the laboratory, consistent with the reactions above (Eqs. 4 and 5). In this study, aegirine was the main mineral in banded REE ore samples, including 18BY62, EB503, and EB126 (Figs. S1C, S2A, and S3A), and it coexists with quartz. Aegirine in the Bayan Obo REE ores has been proposed to be related to fenitization (Liu et al., 2018a), whereby silicon is extracted from country rocks into the fluid during fenitization in the form of SiF_4 and SiF_6^{2-}. Finally, the silicon fluorite from fenitization is precipitated as quartz through the metasomatic process (Eqs. 1 and 2) (Fig. 4A).

Theoretical Simulation

Based on petrographic evidence, a reasonable hypothesis is that the quartz in both banded
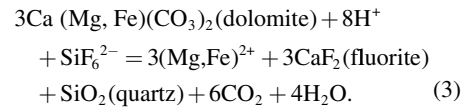
Initial fluids exsolved from the silicon-bearing carbonatite magma may contain silicon fluoride species in the form of SiF_4 and SiF_6^{2-} (Fig. 4A). Due to the instability of silicon fluoride species, SiF_4 and SiF_6^{2-} would be hydrolyzed and produce quartz under specific conditions (Rees and Hudleston, 1936; De Hoog et al., 2005). These reactions are:

$$3SiF_4 + 2H_2O = SiO_2(quartz) + 2H_2SiF_6, \quad (1)$$

and

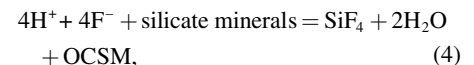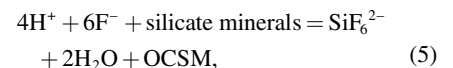$$SiF_6^{2-} + 2H_2O = 6F^- + SiO_2(quartz) + 4H^+. \quad (2)$$

The reaction of fluoride-rich fluids with carbonatite involves a change in pH, which would accelerate the process of hydrolysis of silicon fluoride and further lead to the precipitation of fluoride-bearing minerals, such as fluorite and bastnäsite (Migdisov and Williams-Jones, 2014). One of the reactions can be expressed as follows:
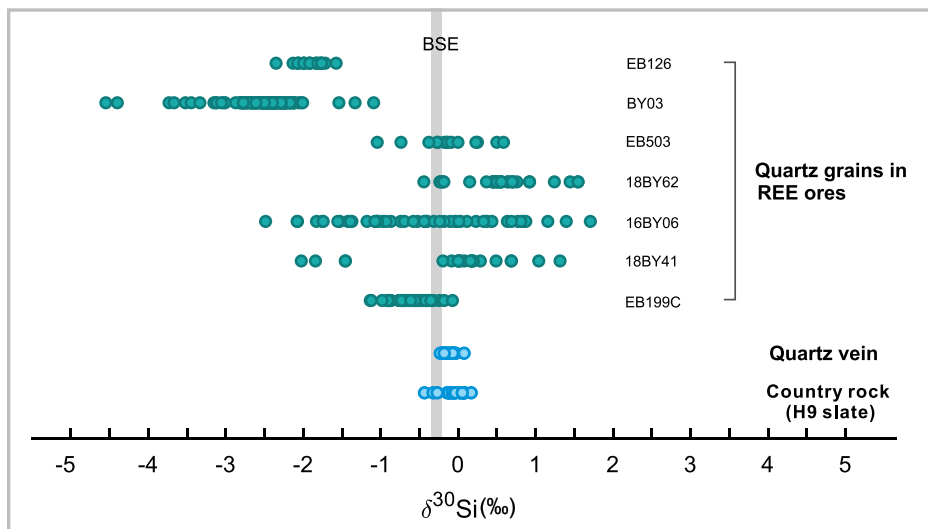
Figure 3. Range of Si isotope compositions of quartz grains in rare earth element (REE) ores, quartz from country rocks, and late quartz vein. Bulk silicate earth (BSE) (δ^{30}Si = $-0.29‰ \pm 0.07‰$) is shown for comparison.

REE ores and carbonatite at Bayan Obo is a product of fluid reactions related to fluoride. However, it is unclear whether the involvement of silicon fluoride species in these fluid reactions could result in the significant range of δ^{30}Si from $-4.55‰$ to $1.71‰$ in quartz, as recorded above.

In theory, Si isotopes fractionate when Si-O bonds and Si-F bonds break or form due to their difference in bond strength. Equilibrium Si isotope fractionation between $SiF_4(g)$, $SiF_6^{2-}(aq)$, and quartz is shown using the Bigeleisen-Mayer equation (Fig. 4B). Theoretical calculations

showed that $SiF_4(g)$ prefers ^{30}Si, whereas the $SiF_6^{2-}(aq)$ prefers ^{28}Si during equilibrium fractionation (Fig. 4B). If it is considered that (1) quartz is the final product of silicon fluoride, (2) there is equilibrium fractionation, and (3) the δ^{30}Si value of bulk silicate earth (BSE) is accepted as the initial point, then the theoretical range of Si isotope values for quartz formed at 300 °C should vary from $-4.29‰$ to $3.01‰$. These theoretical Si results for 300 °C (or even 400 °C; Smith and Henderson, 2000) cover the range of δ^{30}Si variations recorded in quartz at Bayan Obo, and, therefore, it is reasonable to conclude that quartz in the dolomite and REE ores is the product of a series of fluorine-rich hydrothermal reactions as discussed above.

The overall δ^{30}Si values of quartz in carbonatite and banded REE ores at Bayan Obo show a negative shift, with Wei et al. (1994) also reporting a lower range of δ^{30}Si values of REE ores from $-1.8‰$ to $-0.3‰$, which is lighter than values of sedimentary rocks and igneous rocks. The model presented above suggests that escape of part of the $SiF_4(g)$ with heavier δ^{30}Si values from the cooling hydrothermal system (Fig. 4A) could explain the negative shift in Si isotope compositions at Bayan Obo.

IMPLICATIONS

The large Si isotopic fractionations in Bayan Obo carbonatites and REE orebodies demonstrate the existence of silicon fluoride in fluids derived from carbonatite magma. The formation of silicon fluoride in such magmatic-hydrothermal fluids can potentially enhance the solubility of silica and decrease the silica activity in carbonatite magma. This may have important implications for REE mineralization. Apatite is an important REE-hosting mineral in carbonatite magmas, where REEs are more compatible in apatite with high SiO_2 content (Hammouda et al., 2010). Exsolved initial magmatic-hydrothermal fluids from carbonatite magmas have the capacity to lower silicon activity, which then hinders the ability of apatite to capture REEs in the carbonatite magma and instead facilitates the transport of REEs into the fluids (Anenburg et al., 2020). In addition to this mechanism for REE enrichment in carbonatite magmas, the interaction between fluorine-rich fluid and country rocks during fenitization is accompanied not only by the addition of silica, but also by alkali loss, which has the potential to even further promote the deposition of REE minerals during carbonatite-related mineralization (Anenburg et al., 2020).
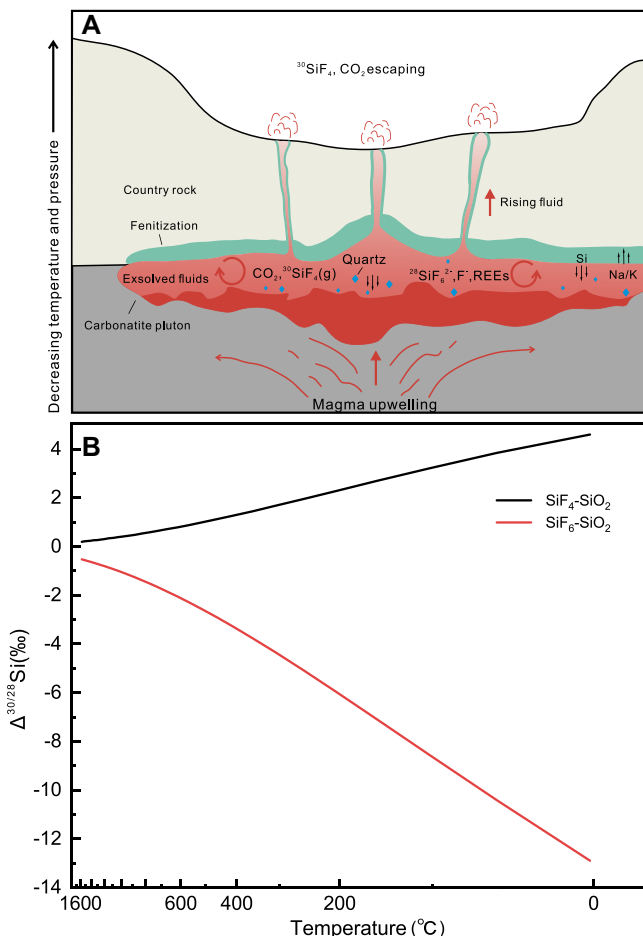
Figure 4. (A) Schematic model illustrating formation of quartz in carbonatite systems. (B) Theoretical calculation results for equilibrium Si isotope fractionation between gaseous SiF_4, aqueous SiF_6^{2-}, and SiO_2.

REFERENCES CITED

Anenburg, M., Mavrogenes, J.A., Frigo, C., and Wall, F., 2020, Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica: Science Advances, v. 6, no. 41, https://doi.org/10.1126/sciadv.abb6570.

Anenburg, M., Broom-Fendley, S., and Chen, W., 2021, Formation of rare earth deposits in carbonatites: Elements, v. 17, no. 5, p. 327–332, https://doi.org/10.2138/gselements.17.5.327.

Barker, D.S., 2001, Calculated silica activities in carbonatite liquids: Contributions to Mineralogy and Petrology, v. 141, no. 6, p. 704–709, https://doi.org/10.1007/s004100100281.

Chao, E.C., Back, J., Minkin, J., Tatsumoto, M., Junwen, W., Conrad, J., McKee, E., Zonglin, H., Qingrun, M., and Shengguang, H., 1997, The Sedimentary Carbonate-Hosted Giant Bayan Obo REE-Fe-Nb Ore Deposit of Inner Mongolia, China: A Cornerstone Example for Giant Polymetallic Ore Deposits of Hydrothermal Origin: U.S. Geological Survey Bulletin 2143, 65 p., https://doi.org/10.3133/b2143.

Chebotarev, D.A., Veksler, I.V., Wohlgemuth-Ueberwasser, C., Doroshkevich, A.G., and Koch-Müller, M., 2018, Experimental study of trace element distribution between calcite, fluorite and carbonatitic melt in the system $CaCO_3 + CaF_2 + Na_2CO_3 \pm Ca_3(PO_4)_2$ at 100 MPa: Contributions to Mineralogy and Petrology, v. 174, no. 1, https://doi.org/10.1007/s00410-018-1530-x.

De Hoog, J.C., Van Bergen, M.J., and Jacobs, M.H., 2005, Vapour-phase crystallisation of silica from SiF_4-bearing volcanic gases: Annals of Geophysics, v. 48, no. 4–5, p. 775–785, https://doi.org/10.4401/ag-3233.

Doroshkevich, A.G., Viladkar, S.G., Ripp, G.S., and Burtseva, M.V., 2009, Hydrothermal REE mineralization in the Amba Dongar carbonatite complex, Gujarat, India: Canadian Mineralogist, v. 47, no. 5, p. 1105–1116, https://doi.org/10.3749/canmin.47.5.1105.

Elliott, H.A.L., Wall, F., Chakhmouradian, A.R., Siegfried, P.R., Dahlgren, S., Weatherley, S., Finch, A.A., Marks, M.A.W., Dowman, E., and Deady, E., 2018, Fenites associated with carbonatite complexes: A review: Ore Geology Reviews, v. 93, p. 38–59, https://doi.org/10.1016/j.oregeorev.2017.12.003.

Giebel, R.J., Parsapoor, A., Walter, B.F., Braunger, S., Marks, M.A.W., Wenzel, T., and Markl, G., 2019, Evidence for magma–wall rock interaction in carbonatites from the Kaiserstuhl volcanic complex (southwest Germany): Journal of Petrology, v. 60, no. 6, p. 1163–1194, https://doi.org/10.1093/petrology/egz028.

Hammouda, T., Chantel, J., and Devidal, J.-L., 2010, Apatite solubility in carbonatitic liquids and trace element partitioning between apatite and carbonatite at high pressure: Geochimica et Cosmochimica Acta, v. 74, no. 24, p. 7220–7235, https://doi.org/10.1016/j.gca.2010.09.032.

Hao, M., Ma, W., and Chen, L., 2010, The distribution of SiO_2 in Bayan Obo main and east orebodies: Science & Technology of Baotou Steel, v. 3, p. 39–40.

Le Bas, M.J., 2008, Fenites associated with carbonatites: Canadian Mineralogist, v. 46, no. 4, p. 915–932, https://doi.org/10.3749/canmin.46.4.915.

Le Maitre, R., Streckeisen, A., Zanettin, B., Le Bas, M., Bonin, B., Bateman, P., Bellieni, G., Dudek, A., Efremova, S., and Keller, J., editors, 2002, Igneous Rocks: A Classification and Glossary of Terms: Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks: Cambridge, UK, Cambridge University Press, 254 p., https://doi.org/10.1017/CBO9780511535581.

Liu, S., Fan, H.-R., Yang, K.-F., Hu, F.-F., Rusk, B., Liu, X., Li, X.-C., Yang, Z.-F., Wang, Q.-W., and Wang, K.-Y., 2018a, Fenitization in the giant Bayan Obo REE-Nb-Fe deposit: Implication for REE mineralization: Ore Geology Reviews, v. 94, p. 290–309, https://doi.org/10.1016/j.oregeorev.2018.02.006.

Liu, S., Fan, H.-R., Yang, K.-F., Hu, F.-F., Wang, K.-Y., Chen, F.-K., Yang, Y.-H., Yang, Z.-F., and Wang, Q.-W., 2018b, Mesoproterozoic and Paleozoic hydrothermal metasomatism in the giant Bayan Obo REE-Nb-Fe deposit: Constraints from trace elements and Sr-Nd isotope of fluorite and preliminary thermodynamic calculation: Precambrian Research, v. 311, p. 228–246, https://doi.org/10.1016/j.precamres.2018.04.021.

Massuyeau, M., Gardés, E., Morizet, Y., and Gaillard, F., 2015, A model for the activity of silica along the carbonatite-kimberlite-melilitite-basanite melt compositional joint: Chemical Geology, v. 418, p. 206–216, https://doi.org/10.1016/j.chemgeo.2015.07.025.

McPhie, J., Kamenetsky, V., Allen, S., Ehrig, K., Agangi, A., and Bath, A., 2011, The fluorine link between a supergiant ore deposit and a silicic large igneous province: Geology, v. 39, no. 11, p. 1003–1006, https://doi.org/10.1130/G32205.1.

Migdisov, A.A., and Williams-Jones, A.E., 2014, Hydrothermal transport and deposition of the rare earth elements by fluorine-bearing aqueous liquids: Mineralium Deposita, v. 49, no. 8, p. 987–997, https://doi.org/10.1007/s00126-014-0554-z.

Mitra, A., and Rimstidt, J.D., 2009, Solubility and dissolution rate of silica in acid fluoride solutions: Geochimica et Cosmochimica Acta, v. 73, no. 23, p. 7045–7059, https://doi.org/10.1016/j.gca.2009.08.027.

Mori, T., Sato, M., Shimoike, Y., and Notsu, K., 2002, High SiF_4/HF ratio detected in Satsuma-Iwojima volcano's plume by remote FT-IR observation: Earth, Planets, and Space, v. 54, no. 3, p. 249–256, https://doi.org/10.1186/BF03353024.

Newton, R.C., and Manning, C.E., 2000, Quartz solubility in H_2O-NaCl and H_2O-CO_2 solutions at deep crust–upper mantle pressures and temperatures: 2–15 kbar and 500–900 °C: Geochimica et Cosmochimica Acta, v. 64, no. 17, p. 2993–3005, https://doi.org/10.1016/S0016-7037(00)00402-6.

Poitrasson, F., 2017, Silicon isotope geochemistry: Reviews in Mineralogy and Geochemistry, v. 82, no. 1, p. 289–344, https://doi.org/10.2138/rmg.2017.82.8.

Rees, A.G., and Hudleston, L.J., 1936, The decomposition of the fluosilicate ion in aqueous and in aqueous salt solutions: Journal of the Chemical Society (Resumed), v. 1936, p. 1334–1338.

Savage, P.S., Georg, R.B., Williams, H.M., and Halliday, A.N., 2013, The silicon isotope composition of the upper continental crust: Geochimica et Cosmochimica Acta, v. 109, p. 384–399, https://doi.org/10.1016/j.gca.2013.02.004.

Smith, M.P., and Henderson, P., 2000, Preliminary fluid inclusion constraints on fluid evolution in the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China: Economic Geology, v. 95, no. 7, p. 1371–1388, https://doi.org/10.2113/gsecongeo.95.7.1371.

Verplanck, P.L., Van Gosen, B.S., Seal, R.R., and Mc-Cafferty, A.E., 2014, A deposit model for carbonatite and peralkaline intrusion-related rare earth element deposits: U.S. Geological Survey Scientific Investigations Report 2010-5070-J, 58 p., http://dx.doi.org/10.3133/sir20105070J.

Wei, J., Jiang, S., and Wan, D., 1994, Si isotopic compositions of the Baiyun Obo rare earth and iron deposits in Inner Mongolia: Acta Geoscientica Sinica, v. 15, no. 1–2, p. 102–110.

Weng, Z., Jowitt, S.M., Mudd, G.M., and Haque, N., 2015, A detailed assessment of global rare earth element resources: Opportunities and challenges: Economic Geology, v. 110, no. 8, p. 1925–1952, https://doi.org/10.2113/econgeo.110.8.1925.

Williams-Jones, A., and Palmer, D., 2002, The evolution of aqueous-carbonic fluids in the Amba Dongar carbonatite, India: Implications for fenitisation: Chemical Geology, v. 185, no. 3–4, p. 283–301, https://doi.org/10.1016/S0009-2541(01)00409-0.

Yang, K., Fan, H., Pirajno, F., and Li, X., 2019, The Bayan Obo (China) giant REE accumulation conundrum elucidated by intense magmatic differentiation of carbonatite: Geology, v. 47, no. 12, p. 1198–1202, https://doi.org/10.1130/G46674.1.

Printed in the USA