Mg, Sr, and O isotope geochemistry of syenites from northwest Xinjiang, China: Tracing carbonate recycling during Tethyan oceanic subduction

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ABSTRACT

Magnesium isotopic compositions of igneous rocks could be potentially used to trace recycling of supracrustal materials. High-δ26Mg granitoids have been previously reported and explained to reflect the involvement of surface weathered materials in their sources. Low-δ26Mg granitoids, however, have not been reported. In this study, we report high-precision Mg isotopic analyses of Cenozoic alkaline syenites and syenogranites from the Kuzigan and Zankan plutons, northwest Xinjiang, China. The Kuzigan syenites were originated from the mantle metasomatized by recycled supracrustal materials, and the syenogranites are differentiated products of the syenites. Both syenites and syenogranites have δ26Mg values (−0.46 to −0.08‰ and −0.41 to −0.17‰, respectively) significantly lighter than the mantle (−0.25 ± 0.07‰, 2SD). No correlation of δ26Mg with either SiO2 or MgO is observed, indicating limited Mg isotope fractionation during alkali magmatic differentiation. The low δ26Mg of the syenites and syenogranites thus reflects a light Mg isotopic source. This, combined with high 87Sr/86Sr ratios (0.70814 to 0.71105) and negative correlation between δ26Mg and δ18O, suggests that the magma source contains recycled marine carbonates. Modeling of the Mg-O-Sr isotopic data indicates that the recycled carbonate is mainly limestone with minor dolostone, suggesting that the metasomatism occurred at depths shallower than 60 to 120 km. Given that the plutons are located at the India–Eurasia collision zone, the carbonate recycling was most likely derived from the subducted Tethyan oceanic crust during the Mesozoic–Cenozoic. Our study suggests that the combined Mg, O, and Sr isotopic studies are powerful for tracing recycled carbonates and identifying their species in mantle sources.

1. Introduction

Warm global climate at Cretaceous–early Cenozoic era was attributed to a high pCO2 level possibly maintained by subduction of Tethyan oceanic crust with pelagic carbonate and subsequent release of CO2 from arc volcanism (Kent and Muttoni, 2008). However, according to the carbon budget in subduction zones, the expelled carbonate from arc volcanism is much less than that subducted, implying that a mass of undissolved carbonate is subducted to the deep mantle (Kerrick and Connolly, 2001). Tracing the recycled carbonates and evaluating their proportions in the mantle becomes an important issue (e.g., Li, 2015).

Recent studies show that Mg isotopic compositions of igneous rocks could be used to trace the recycling of supracrustal materials in the magma source (Shen et al., 2009; Li et al., 2010; Yang et al., 2012; Huang et al., 2015; Wang et al., 2016). Compared with the upper mantle (δ26Mg = −0.25 ± 0.07‰, 2SD; Teng et al., 2010), clastic sedimentary rocks (δ26Mg of −1.64 to +0.92‰; Li et al., 2010; Huang et al., 2013) and carbonates (δ26Mg of −5.60 to −0.66‰; Beinlich et al., 2014; Saenger and Wang, 2014), on average, have heavy and light Mg isotopic compositions, respectively. Therefore, Mg isotopes are an effective tool in distinguishing recycled clastic sediments and carbonates, given that Mg isotopes are not significantly fractionated during high-temperature magmatic processes. Especially, stability of carbonate species (calcite, dolomite, and magnesite) in the mantle via subduction depends on the P-T conditions (Dasgupta and Hirschmann, 2010). Thus, constraining the species of recycled carbonates has a crucial implication for understanding the depth of the recycled carbonates. However, the species of recycled carbonate is difficult to identify by using Mg isotopes alone because all carbonate minerals (e.g., calcite, dolomite, and magnesite) have light Mg isotopic composition (Saenger and Wang, 2014). Nevertheless, carbonate minerals have significantly different Mg and Sr contents but similar O contents, then mixing of calcite, dolomite, and magnesite with the mantle will generate different curves in the plots of Mg versus O and Sr isotopes. Thus, a combination of Mg, Sr, and O isotopes may be an effective approach to identify the species of carbonates and to explore their potential application in tracing deep carbon recycling.

The Pamir syntaxis belongs to the westernmost part of the Himalayan–Tibetan orogen, formed by the Tethyan oceanic subduction and...
the India–Eurasia collision during Paleozoic to Cenozoic. Cenozoic post-
collisional potassic and ultrapotassic igneous rocks are widely distribut-
ed in the middle Pamir (Hacker et al., 2005; Ke et al., 2008; Jiang et al.,
2012). Previous studies proposed that these potassic and ultrapotassic
rocks in Pamir originated from the enriched mantle source related to
the subducted India continent (Pan, 2000; Jiang et al., 2012). Contempo-
raneous ultrapotassic magmatic rocks in Tibet were also generally pro-
posed to be the products of partial melting of the enriched mantle
(Turner et al., 1996; Miller et al., 1999; Nomade et al., 2004; Williams
et al., 2004; Chung et al., 2005; Zhao et al., 2009; Jiang et al., 2012;
Wang et al., 2014a). Therefore, if huge amounts of carbonates were car-
ried into the mantle by subduction of the Tethyan oceanic slabs, the
chemical properties of mantle beneath the Tibetan plateau would
have been modiﬁed by recycled carbonates and then may imprint the
signature on mantle-derived igneous rocks, a hypothesis that can be ex-
amined using Mg-O-Sr isotopes as discussed above.

In this study, we report Mg, O, and Sr isotopic data for ultrapotassic
alkaline syenites and evolved syenogranites from two Cenozoic plutons
(Kuzigan and Zankan) in the Pamir syntaxis, northwestern Xinjiang,
China. The aim of this study is to (i) investigate the behavior of Mg iso-
topes during alkaline magmatic differentiation, which is not addressed
yet, and the origin of the low \( \delta^{26}\text{Mg} \) syenites and syenogranites; (ii)
evaluate the imprint of carbonate recycling in the mantle beneath the
Pamir plateau during the subduction of the Tethyan oceanic slabs; and (iii) explore a way using Mg-O-Sr isotopes to identify recycled carbonate species.

2. Geological setting and samples

The Pamir syntaxis, located in the western Himalayan–Tibetan
orogen, is composed of several distinctive terranes and suture zones
that accreted to the southern margin of Asia during the late Paleozoic–
Mesozoic closure of the Paleo-Tethys Ocean and the Mesozoic–Cenozoic
closure of the Neo-Tethys Ocean (Burtman and Molnar, 1993; Schwab
et al., 2004). The Pamir area is divided into the northern, central, and
southern zone based on the Paleozoic and Mesozoic sutures (Burtman
and Molnar, 1993). To the south, the Indus suture and Shyok suture
were the marks of the ﬁnal India–Eurasia collision in Cenozoic
(Bouilhol et al., 2013).

Cenozoic igneous rocks were widely distributed in the central and
southern Pamir (Ducea et al., 2003; Hacker et al., 2005). The Kuzigan al-
kaline pluton, paralleling the Karakorum fault, is one of this Cenozoic
magmatic belt (Fig. 1a). It is bounded by a Miocene granite pluton
(Karibasheng) (Fig. 1a) to the northeast and gneissic granites of

![Simplified geological map of the eastern Pamir and sample section.](image)

Fig. 1. Simplified geological map of the eastern Pamir and sample section. (a) Geological map modified from Jiang et al. (2012), emphasizing Cenozoic igneous rocks. Inset map shows the location of Kuzigan and Zankan plutons in the Pamir syntaxis. (b) Section map of the Kuzigan alkaline pluton, emphasizing the rock types, contact relationships, and sampling locations.
unknown age to the southwest (Fig. 1b). The Kuzigan pluton is made up of alkaline syenites, syenitoids, and syenogranites, with medium- to coarse-grained aegirine–augite syenites and syenogranites as their representative rocks. The different lithologies have gradual contacts without clear boundaries, indicating a synchronous magmatic activity. SHRIMP U–Pb zircon ages of syenites and syenogranites confirm that they belong to the same magmatic episode at ca. 11 Ma (Ke et al., 2008; Jiang et al., 2012). The Zankan syenitic pluton is another intrusive body of the Cenozoic magmatism belt to the southeast along the Karakorum fault (Fig. 1a). Kuzigan and Zankan plutons were considered to be the products of the synchronous magmatic and tectonic process in the Pamir syntaxis based on the same age (ca. 11 Ma; Pan, 2000), rock type, and geochemical feature (Pan, 2000).

Syenites and syenogranites from the Kuzigan pluton share the same mineral assemblage of potassium feldspar, oligoclase, quartz, aegirine-augite, minor biotite, and rare hornblende. Mineral modes, however, are different, e.g., aegirine-augite are enriched in syenites (6–20% in volume) but depleted in syenogranites (less than 2% in volume). In addition, syenites and syenogranites have similar Sr, Nd, and Pb isotopic compositions (see Table 1 for Sr isotopes, and Ke et al., 2006 and Jiang et al., 2012 for Nd-Pb isotopes). Hence, the same spatial and temporal distribution, the similar mineral assemblage and Sr-Nd-Pb isotopic compositions suggest that syenites and syenogranites from the Kuzigan pluton were from the same source (Pan, 2000; Ke et al., 2006; Jiang et al., 2012). Syenites from the Zankan pluton are medium-grained aegirine–augite syenites with similar texture and mineral assemblage as syenites from the Kuzigan pluton. The gneissic biotite granites from the wall rock are poorly studied, which are composed of potassium feldspar, oligoclase, quartz, and minor biotite.

Previous studies suggested that the Kuzigan pluton were derived from the hybridized lithospheric mantle and could not be produced by partial melting of the thickened lower crust or subducted slab based on the following arguments (Jiang et al., 2012): (1) Melts derived by partial melting of thickened lower crust or of subducted slab would show the adakitic affinity, which, however, is not observed in the Kuzigan pluton; (2) the Kuzigan pluton has much higher Ba (2200–9100 ppm) and Sr (840–3100 ppm, most >1100 ppm) contents than those of the common granites, suggesting that the source of Kuzigan pluton is more enriched in Ba and Sr than the source of common granites; and (3) high Ba/Sr (10–34) and low Rb/Sr (0.08–0.26) ratios suggest a metasomatized mantle source with the presence of both phlogopite and amphibole.

Twelve syenites and nine syenogranites were collected along a geological section from the Kuzigan pluton. Two syenite samples from the Zankan pluton for comparison and two gneissic granites from the wall rock are selected. All samples collected in this study are fresh without secondary alteration.

### 3. Analytical methods

#### 3.1. Major elements

Major elements were determined by a Prodigy inductively coupled plasma-optical emission spectroscopy (ICP-OES) using standard methods at the China University of Geosciences, Beijing (CUGB). Loss on ignition (LOI) was determined gravimetrically after heating the samples at 1000 °C for half hour. The analytical uncertainties were better than 1% after repeated measurements of rock reference standards AGV-2 and GBW07103.

#### 3.2. Oxygen and strontium isotopes

Oxygen isotopes were analyzed using a Finnigan MAT-253F EM mass spectrometer at the Key Laboratory for Isotope Geology, Ministry of Land and Resources. Oxygen isotopes were processed by the BrF5 method described by Clayton and Mayeda (1963) and then converted into δ 18O values relative to the Vienna Standard Mean Ocean Water (SMOW).

Strontium isotopes were analyzed by using a Neptune Plus MC-ICP-MS at the Isotope Geochemistry Laboratory of the China University of Geosciences, Beijing. Strontium isotope fractionation is corrected to 86Sr/88Sr = 0.1194. Data are corrected for 87Rb interference by the measured 85Rb abundance. A 200-ppb Sr solution typically produced 5.0 V for 88Sr and 0.004 V for 86Sr signal (with a 1Ω resistor for the Faraday cups) with 85Rb/86Sr less than 8 × 10^-11. Correction of the interference of 85Rb breaks down only when 85Rb/86Sr is less than 1 × 10^-3. Therefore, the separation of Sr from Rb was efficient, and 87Sr/86Sr of samples are reliable in this study. NBS987 measured during the course of this study yields 87Sr/86Sr = 0.710262 ± 16 (2SD, n = 7). The BHVO-2 gives a value of 87Sr/86Sr = 0.703458 ± 10 (2SD). The total blank for Sr isotope analysis is less than 1.0 ng.

#### 3.3. Magnesium isotopes

Magnesium isotopes were analyzed using a Nu Plasma MC-ICP-MS at the Isotope Geochemistry Laboratory of the China University of Geosciences, Beijing. The experiment parameters applied in the two laboratories at UA and CUGB are shown in Table 2. All geostandards and three samples that were measured in both of the labs yield consistent results within quoted errors (Tables 3 and 4).

#### 3.3.1. Analytical method at UA

The analytical method in UA has been previously reported (e.g., Yang et al., 2009; Li et al., 2010; Teng and Yang, 2014; Teng et al., 2015a).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>LOI</th>
<th>δ 18O</th>
<th>Sr isotopic compositions of syenites and syenogranites from the Kuzigan and Zankan plutons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuzigan syenites</td>
<td>0.17</td>
<td>0.22</td>
<td>0.26</td>
<td>0.31</td>
<td>0.39</td>
<td>0.42</td>
<td>0.48</td>
<td>0.52</td>
<td>0.58</td>
</tr>
<tr>
<td>Kuzigan syenogranites</td>
<td>0.18</td>
<td>0.23</td>
<td>0.27</td>
<td>0.32</td>
<td>0.39</td>
<td>0.42</td>
<td>0.48</td>
<td>0.52</td>
<td>0.58</td>
</tr>
</tbody>
</table>

For tables, please use the LaTeX table markup.
same sample solution (3:1) and re-dissolved by concentrated HNO3. The chemical separation of concentrated HF:HNO3, then a concentrated HCl:HNO3 mixture and CUGB Mg isotopic compositions of synthetic solutions and reference materials measured at UA and CUGB Mg is an ultrapure single elemental standard solution from China Iron and Steel Research Institute.

Table 2
<table>
<thead>
<tr>
<th>Lab</th>
<th>UA</th>
<th>CUGB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>Nu Plasma MC-ICP-MS</td>
<td>Neptune Plus MC-ICP-MS</td>
</tr>
<tr>
<td>Spray chamber</td>
<td>Quartz cyclonic spray chamber</td>
<td>Scott double pass quartz glass spray chamber</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>100 µl/min glass concentric self-aspiration nebulizer</td>
<td>50 µl/min PFA self-aspiration micro nebulizer</td>
</tr>
<tr>
<td>Autosampler</td>
<td>SC-2 from ESI</td>
<td>Cetac ASX-110</td>
</tr>
<tr>
<td>Interface</td>
<td>Nickel</td>
<td>Nickel</td>
</tr>
</tbody>
</table>

The parameters of UA are from Yang et al. (2009), Teng et al. (2010), and Teng and Yang (2014). 

| Faraday cups | L4, Ax, and H5 | L3, C, H3 |
| resolution | Low-resolution mode | Low-resolution mode |
| Typical 26Mg sensitivity | 2.5 to 4.5 V/100 ppb | 4.5 to 8 V/400 ppb |
| Analytical section | 4 blocks and 40 cycles for each block | 4 or 6 blocks and 30 cycles for each block |
| Background <1 x 10^-4 V | <2 x 10^-4 V |
| 26Mg signal | | |
| Blank | <10 ng | <10 ng |
| In-run precision | ±0.02% (2SD) | ±0.02% (2SD) |
| Internal precision | <0.1% (2SD) | <0.1% (2SD) |
| External precision | 0.07% (2SD) for δ26Mg | 0.06% (2SD) for δ26Mg |

Briefly, the whole rock powder (200 mesh) was dissolved in a 3:1 mixture of concentrated HF:HNO3, then a concentrated HCl:HNO3 mixture (3:1) and re-dissolved by concentrated HNO3. The chemical separation of Mg was achieved using iron exchange resin AG50W-X8 (Bio-Rad 200–400 mesh) following the procedure described by Teng et al. (2007). The same column procedure was repeated twice with the whole procedure blank less than 10 ng. The long-term external precision was ±0.06% for δ26Mg and ±0.07% for δ26Mg (2SD) (Teng et al., 2010, 2015a, b).

Table 3
<table>
<thead>
<tr>
<th>Lab</th>
<th>Lab ID</th>
<th>δ26Mg 2SD</th>
<th>δ26Mg 2SD</th>
<th>δ26Mg 2SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA</td>
<td>KH Olivine</td>
<td>-0.27 0.08</td>
<td>-0.15 0.05</td>
<td>0.05 4</td>
</tr>
<tr>
<td>K1 Olivine</td>
<td>-0.31 0.06</td>
<td>-0.15 0.05</td>
<td>0.05 4</td>
<td></td>
</tr>
<tr>
<td>K1 Olivine</td>
<td>-0.27 0.06</td>
<td>-0.17 0.06</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Granite</td>
<td>0.02 0.08</td>
<td>0.01 0.05</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Granite</td>
<td>-0.04 0.07</td>
<td>-0.02 0.05</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Granite</td>
<td>-0.03 0.07</td>
<td>-0.01 0.06</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Granite</td>
<td>-0.07 0.05</td>
<td>-0.03 0.01</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Chondrite</td>
<td>-0.07 0.07</td>
<td>-0.03 0.04</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Mg-1</td>
<td>-0.08 0.07</td>
<td>-0.01 0.04</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>IL-Clinopyroxene</td>
<td>-0.02 0.04</td>
<td>-0.02 0.05</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>BHVO-2</td>
<td>-0.20 0.07</td>
<td>-0.10 0.04</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Seawater</td>
<td>-0.83 0.09</td>
<td>-0.43 0.06</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>PCC-1</td>
<td>-0.23 0.06</td>
<td>-0.10 0.01</td>
<td>0.01 3</td>
<td></td>
</tr>
<tr>
<td>DST-1</td>
<td>-0.30 0.01</td>
<td>-0.13 0.01</td>
<td>0.01 4</td>
<td></td>
</tr>
<tr>
<td>CUGB</td>
<td>GSB Mg</td>
<td>-1.05 0.03</td>
<td>-2.04 0.04</td>
<td>0.04 4</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>-0.25 0.06</td>
<td>-0.13 0.04</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>BCR-2</td>
<td>-0.19 0.05</td>
<td>-0.10 0.03</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>AGV-2</td>
<td>-0.17 0.05</td>
<td>-0.08 0.03</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>Seawater</td>
<td>-0.83 0.02</td>
<td>-0.42 0.03</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>PCC-1</td>
<td>-0.25 0.04</td>
<td>-0.13 0.02</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>DST-1</td>
<td>-0.32 0.04</td>
<td>-0.16 0.04</td>
<td>0.04 4</td>
<td></td>
</tr>
<tr>
<td>DST-2</td>
<td>-0.33 0.04</td>
<td>-0.15 0.04</td>
<td>0.04 4</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2. Analytical method at the CUGB

The chemical procedure used in CUGB is the same as that in UA. The recovery of Mg is up to 99.5%–99.9%, and the whole procedure blank is less than 10 ng as well. Mg isotope analysis, however, was conducted using a Neptune MC-ICP-MS (Table 2). The detailed instrument parameters at the CUGB have been previously reported by Liu et al. (2014b) and He et al. (2015). Hence, we report the parts relevant to Mg isotope analysis in details below.

All samples and standards were introduced to the Ar plasma in 3% HNO3 using a Scott double pass quartz glass spray chamber and a low-flow 50 µl/min PFA self-aspiration micro nebulizer, with help of a Cetac ASX-110 autosampler. The sample introduction system was washed with 3% HNO3 for 2 min after each measurement to avoid cross-contamination. Mg isotopes were determined in a low-mass resolution mode under wet plasma conditions. The isobaric interferences,
such as $^{12}$C$^{12}$C, $^{12}$C$^{14}$N, $^{23}$NaH, and $^{25}$Mg$^{2+}$ have been checked at the low-resolution mode. They are unresolvable by signal peaks of 3% HNO$_3$ (the blank solution) and thus could be negligible. $^{24}$Mg, $^{25}$Mg, and $^{26}$Mg ion beams are simultaneously collected in L3, C, and H3 Faraday cups. Each measurement consists of a 3s idle time and 30 cycles of 4.19 or 8.39 s integration time. About 400 ppb Mg concentration typically produced 4.5–8 V $^{24}$Mg signal (with a 1011–1 resistor for the Faraday cups) (Table 2). The Mg isotope ratios are reported related to the Dead Sea metal Mg standard (DSM3) using the following expression:

$$\delta^{26}\text{Mg}(‰) = \left(\frac{^{26}\text{Mg}}{^{24}\text{Mg}}\right)_{\text{sample}} \times 1000 - \left(\frac{^{26}\text{Mg}}{^{24}\text{Mg}}\right)_{\text{DSM3}}$$

The sample-standard sequence for each sample was repeated 4 or 6 times to get a better reproducibility and accuracy. The internal precision, calculated by 4 or 6 times duplicate measurement within an analytical session, is generally better than ±0.1‰ (2SD). During a typical analytical session, the in-house standard GSB Mg with known values (an ultrapure single elemental standard solution from China Iron and Steel Research Institute) and at least one rock reference standard (e.g., BHVO-2, BCR-2, AGV-2) were analyzed with unknown samples to check long-term reproducibility of the method.

The long-term external precision (2SD) is ±0.06‰ for $\delta^{26}$Mg and ±0.05‰ for $\delta^{25}$Mg, based on the following analyses since June 2012 (Fig. 2): (1) Mg isotope analyses of pure Mg solutions without column chemistry (GSB Mg: $\delta^{26}$Mg = −2.04 ± 0.04‰, $\delta^{25}$Mg = −1.05 ± 0.03‰, n = 58) and (2) analyses of reference materials from USGS processed through column chemistry twice, yielding $\delta^{26}$Mg = −0.25 ± 0.06‰ and $\delta^{25}$Mg = −0.13 ± 0.04‰ for BHVO-2 (n = 48), $\delta^{26}$Mg = −0.19 ± 0.05‰ and $\delta^{25}$Mg = −0.10 ± 0.03‰ for BCR-2 (n = 19), $\delta^{26}$Mg = −0.17 ± 0.05‰ and $\delta^{25}$Mg = −0.08 ± 0.03‰ for AGV-2 (n = 13) (Table 3). $\delta^{26}$Mg values of BCR-2 are identical to the literature data within the analytical uncertainty (e.g., Huang et al., 2011). $\delta^{26}$Mg values of AGV-2 obtained in this study are identical to the data reported by An et al. (2014) but slightly heavier than that reported by Lee et al. (2014). $\delta^{26}$Mg values of BHVO-2, PCC-1, DST-1, and seawater analyzed in CUGB are well consistent with the recommended values within uncertainty (Teng et al., 2015a) (Table 3).

4. Results

4.1. Major element compositions

The major element compositions of syenites and syenogranites from the Kuzigan and Zankan plutons are reported in Table 1. Chemical compositions are extensively variable in the Kuzigan pluton, with SiO$_2$ ranging from 51.60 to 74.81 wt.% and MgO varying from 0.10 to 5.54 wt.%. Sample 018R4 with the lowest SiO$_2$ content (51.60 wt.%) is classified as syenite based on the mineral assemblage (60% potassium feldspar, 3% oligoclase, 22% aegirine–augite, 10% biotite, and 5% melanite). The Kuzigan and Zankan plutons are characterized by high K$_2$O contents (3.74 to 11.74 wt.%). In particular, the syenites are highly enriched in K$_2$O with K$_2$O/Na$_2$O mostly >2, showing affinities with shoshonitic and ultrapotassic igneous rocks in Tibet (Jiang et al., 2012; Zhao et al., 2009; Liu et al., 2014a).

4.2. Oxygen and strontium isotopic compositions

Oxygen and strontium isotopic data are reported in Table 1. Samples from the Kuzigan pluton have high $\delta^{18}$O values from 8.6 to 11.6‰, with an average of 10.2‰, $\delta^{87}$Sr/$^{86}$Sr values of the syenite (8.6 to 10.4‰) are slightly lighter than those of the syenogranites (10.0 to 11.6‰). Syenites from the Zankan pluton also display heavy O isotopic compositions (10.1 and 11.1‰), slightly heavier than those of the Kuzigan pluton. The wall rock, gneissic granites, is the lightest among samples analyzed in this study ($\delta^{18}$O = 8.5‰).

The syenites and syenogranites have relatively constant Sr isotopic ratios over the wide SiO$_2$ range. In detail, the syenites show a larger range of $^{87}$Sr/$^{86}$Sr ratios (0.708143 to 0.711045) than that of syenogranites (0.709368 to 0.710284). Two syenites from the Zankan pluton have similar Sr isotopic ratios as those from the Kuzigan pluton (Table 1).

4.3. Magnesium isotopic compositions

Magnesium isotopic data of syenites and syenogranites are presented in Table 4. In a $\delta^{26}$Mg versus $\delta^{25}$Mg plot, samples and reference materials together yield a slope of 0.513. Several samples analyzed at UA were also analyzed at CUGB for comparison. The results from the two

![Fig. 2](https://example.com/fig2.png) Magnesium isotopic compositions of BHVO-2, BCR-2, AGV-2, and GSB Mg (an ultrapure single elemental standard solution from China Iron and Steel Research Institute) since 06/2012. The black horizontal line represents the average $\delta^{26}$Mg. Error bars represent 2SD uncertainties. Data are reported in Table 3.
Mg isotopic compositions of syenites and syenogranites from the Kuzigan pluton vary from $-0.40$ to $-0.26\%$, with an average of $-0.35 \pm 0.08\%$, and from $-0.41$ to $-0.17\%$ with an average of $-0.32 \pm 0.14\%$, respectively. This is in contrast to the heavy $\delta^{26}\text{Mg}$ in I- and A-type granitoids (Shen et al., 2009; Li et al., 2010), and the mantle-like Mg isotopic compositions in I-type granites (Liu et al., 2010) (Fig. 3). Despite overlapping, $\delta^{26}\text{Mg}$ values of the syenogranites are on average slightly heavier than those of the syenites (Fig. 3). Two syenites from the Zankan pluton have slightly lighter Mg isotopic compositions ($-0.37$ and $-0.46\%$) than those from the Kuzigan region (Table 4). The wall rocks, gneissic granites, have mantle-like $\delta^{26}\text{Mg}$ values of $-0.26\%$ and $-0.27\%$ (Table 4).

5.1. The lack of Mg isotope fractionation during alkaline magmatic differentiation

Equilibrium Mg isotope fractionation is limited during crystal–melt differentiation of komatitits, basaltic, and granitic magmas, consistent with the undetectable Mg isotopic differences among common silicate minerals (olivine, pyroxene, hornblende, and biotite) (Handler et al., 2009; Yang et al., 2009; Young et al., 2009; Dauphas et al., 2010; Liu et al., 2010, 2011; Pogge von Strandmann et al., 2011; Xiao et al., 2013; Hu et al., 2015). To date, the behavior of Mg isotope fractionation during magmatic differentiation in the alkaline syenitic system is unclear.

5.2. Origin of low $\delta^{26}\text{Mg}$ and high $\delta^{18}\text{O}$ in syenites and syenogranites

Given the limited Mg isotope fractionation during alkaline magmatic differentiation, other processes that could potentially produce low-$\delta^{26}\text{Mg}$ signatures include (1) assimilation by wall rocks, (2) thermal and chemical diffusion within the magma chamber and/or around the contact boundaries (Richter et al., 2008, 2009; Teng et al., 2008, 2011; Huang et al., 2009; Lundstrom, 2009), and/or (3) heterogeneous source involved by low-$\delta^{26}\text{Mg}$ materials (Yang et al., 2012; Huang et al., 2015).

Extensive assimilation by wall rocks with light Mg and heavy O isotopic compositions may lower $\delta^{26}\text{Mg}$ and increase $\delta^{18}\text{O}$ values of the syenites and syenogranites. However, xenoliths of wall rocks have not been found yet even along the contact zones, indicating a lack of strong assimilation. The wall rocks, gneissic granites, have heavier Mg isotopic compositions ($-0.26\%$ and $-0.27\%$) and lighter O isotopic compositions (8.5%) than the syenites and syenogranites, excluding the possibility that the light $\delta^{26}\text{Mg}$ and heavy $\delta^{18}\text{O}$ in the syenites and syenogranites were caused by wall rock assimilation. In addition, the lack of any major shift in Mg isotopic compositions along the sample profile precludes extensive assimilation of wall rocks during magma ascent, differentiation, and emplacement (Fig. 6).

Chemical and thermal diffusion could produce large Mg isotope variation under a chemical or temperature gradient (Richter et al., 2008, 2009; Huang et al., 2009; Teng et al., 2011). For a magmatic body, the contact boundary is a place where the temperature and chemical gradients are most likely maintained. If diffusion was responsible for the observed Mg isotope variation, then the $\delta^{26}\text{Mg}$ values are expected to correlate with the distance to the contact boundary. However, the low-$\delta^{26}\text{Mg}$ samples are not only distributed along the boundaries but also occur over the whole ~9 km long geological section cross the Kuzigan pluton (Fig. 6). Furthermore, the negative correlation between Mg and O isotopes is difficult to explain by thermal diffusion (Fig. 7). During thermal diffusion, heavy isotopes always tend to be enriched at the cold end relative to light isotopes, resulting in two different stable isotopic systems that correlate positively with each other (Richter et al., 2008, 2009; Huang et al., 2009; Teng et al., 2011). Therefore, the negative correlation between $\delta^{26}\text{Mg}$ and $\delta^{18}\text{O}$ rules out chemical or thermal
diffusion as the cause of the low $\delta^{26}\text{Mg}$ in the Kuzigan syenites and syenogranites.

The most likely mechanism for the low-$\delta^{26}\text{Mg}$ in the Kuzigan syenites and syenogranites is source heterogeneity, as shown by the O isotopic data. Syenites and syenogranites from the Kuzigan and Zankan plutons have heavy O isotopic compositions compared with the normal mantle ($\delta^{18}\text{O} = 5.5$‰; Hoefs, 2009). Magmatic differentiation could increase $\delta^{18}\text{O}$ of syenogranites because quartz is the most $^{18}\text{O}$-rich mineral compared to feldspar and clinopyroxene (Hoefs, 2009). Nonetheless, the heavy O isotopic compositions of syenites should not be affected by magmatic differentiation and thus reflect either crustal contamination or source heterogeneity. Crustal contamination would increase $\delta^{18}\text{O}$ and $87\text{Sr}/86\text{Sr}$ as well as SiO$_2$ and Sr contents and lead to positive correlations between $\delta^{18}\text{O}$ and SiO$_2$ and between $87\text{Sr}/86\text{Sr}$ and Sr, which are not observed here. Therefore, the high $\delta^{18}\text{O}$ values of these syenites must inherit from their mantle source that had been affected by sedimentary or metasedimentary protoliths. The negative correlation between $\delta^{26}\text{Mg}$ and $\delta^{18}\text{O}$ strongly suggests that carbonates are the most likely component in their mantle source based on their extremely light Mg and heavy O isotopic compositions (Fig. 7). The sedimentary signature is also reflected in the high $87\text{Sr}/86\text{Sr}$ (Table 1) and extreme LILE enrichment (e.g., Ba and Sr) (Ke et al., 2006; Jiang et al., 2012).

5.3. Species of recycled carbonate and mantle source depth

Stability of subducted carbonate species in the mantle strongly depends on the P-T conditions. Dolomite could dissociate into aragonite + magnesite under high P-T conditions (e.g., at $T = 700$ °C, $P > 5.3–6.0$ GPa) (Sato and Katsura, 2001). Calcite is unstable in the presence of enstatite and will transform to dolomite + diopside assemblage under conditions of $P = 2.3$ GPa, $T = 1000$ °C (Kushiro, 1975). Therefore, constraining the species of recycled carbonates has an implication for understanding the mantle source depth. However, to date, how to identify the species of recycled carbonate is poorly known.

Calcite and dolomite have similar Mg, O, and Sr isotopic compositions, but the latter has heavy Mg isotopic composition and higher Mg
Syenogranite Wall rock 0.1 0.4 (Fig. 8a). This amount of Indian sediments is contradictory to the model-order to calcitic and dolomitic marbles in subduction zone rather than sediments. Mg isotopic compositions of ultrahigh pressure metamorphic (UHPM) carbonates are used for modeling calculation (Wang et al., 2014b). Recent studies found that δ26Mg values of calcite-rich carbonates vary significantly lower MgO contents, while the dolomite carbonates tend to greatly through carbonate-silicates interaction during subduction due to their low MgO contents, while the dolomite carbonates tend to keep their original δ26Mg signature (Wang et al., 2014b). Therefore, Mg isotopic compositions of ultrahigh pressure metamorphic (UHPM) calcitic and dolomitic marbles in subduction zone rather than sedimentary carbonates are used for modeling calculation (Wang et al., 2014b).

The Mg-O isotope modeling shows that mixing of a small amount of dolostone with the depleted mantle (DMM) could significantly lower the δ26Mg values and increase the δ18O values. However, dolostone alone makes the slope of the mixing line too sharp to fit the Mg and O isotopic compositions of syenites. Involvement of the Indian sediments (clastic sediments) or limestone could overlap the observed δ26Mg variation (Figs. 8 and 9). However, unrealistically large amount of the Indian sediments (from 74% to 90% relative to dolostone) is required in order to fit the data by mixing dolostone, Indian sediments, and DMM (Fig. 8a). This amount of Indian sediments is contradictory to the modeling result based on Mg and Sr isotopic compositions in Fig. 8b, in which a maximum 30% of Indian sediments is needed.

If the recycled carbonates contain both dolostone and limestone, then the limestone must be a major component (65% to 90%) to fit the Mg and O isotopic data (Fig. 9a). However, involvement of carbonates (limestone + dolostone) alone could not account for Sr isotopic compositions of the samples (Fig. 9b). Hence, the clastic sediments (e.g., Indian sediments) with heavy Mg isotopic composition and high 87Sr/86Sr are required. These clastic sediments were probably carried into the mantle.

### Table 5

<table>
<thead>
<tr>
<th>Elemental Composition</th>
<th>δ26Mg</th>
<th>δ18O</th>
<th>δ87Sr/86Sr</th>
<th>MgO (wt.%)</th>
<th>Sr (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMM</td>
<td>0.25</td>
<td>5.5</td>
<td>0.7025</td>
<td>38</td>
<td>7.7</td>
</tr>
<tr>
<td>Dolostone</td>
<td>2.17</td>
<td>22.0</td>
<td>0.7080</td>
<td>23</td>
<td>222</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.66</td>
<td>22.0</td>
<td>0.7080</td>
<td>0.5</td>
<td>340</td>
</tr>
<tr>
<td>Indian sediments</td>
<td>0.05</td>
<td>17.0</td>
<td>0.8000</td>
<td>2.3</td>
<td>88</td>
</tr>
</tbody>
</table>

DMM is the depleted mantle. The δ18O and δ26Mg (−0.25 ± 0.07‰) values of DMM are from Hoefs (2009) and Teng et al. (2010), respectively. Other data of the DMM are taken from Workman and Hart (2005). Dolostone is the Cretaceous dolostones of Cuogin basin, Qinhai-Tibet Plateau (Li et al., 2008). In order to avoid the post-diagenetic effect on Sr isotopic composition of the dolostone, 87Sr/86Sr ratio of the Cretaceous sea water in the south Tibet (0.708; Huang et al., 2004) is used to represent that of the dolostones. δ26Mg value of dolostone is an average Mg isotopic composition of ultrahigh pressure metamorphic (UHPM) dolomitic marbles from Wang et al. (2014b). Other data of the dolostone are taken from Li et al. (2008). Limestone is the Cretaceous pure biogenic limestones of Nyanang-Gamba, Tibet. The δ18O value of Gamba limestones is from Li et al. (2005). 87Sr/86Sr ratio of the Cretaceous sea water in the south Tibet (0.708; Huang et al., 2004) is used to represent that of the limestones. MgO content is from Chen and Dong (1982). The Sr concentration is from Zong et al. (1982). The δ26Mg value is the average of Mg isotopic compositions of UHPM calcitic marbles from Wang et al. (2014b).

Fig. 6. Relationship of δ26Mg values and sample spatial distribution. The dashed line represents δ26Mg value of the Earth (−0.25‰; Teng et al., 2010). The gray strips are contact boundaries based on the sample section (Fig. 1b).

Fig. 7. Plot of δ26Mg versus δ18O of syenites and syenogranites from the Kuzigan and Zankan alkaline intrusions. Data are from Tables 1 and 4.

Fig. 8. (a) Mg-O isotopes modeling for mixing of the depleted mantle (DMM), dolostone, and the Indian sediment. (b) Mg-Sr isotopes modeling for mixing of the DMM, dolostone, and the Indian sediment. The label on each curve is proportions of dolostone:Indian sediment. Parameters and data source are reported in Tables 1, 4, and 5. Points on mixing curves are at 10% intervals.
source by subducted India continent during the India--Eurasia collision. The Mg-Sr isotope modeling shows that all samples lie along mixing lines between the DMM and a mixture of dolostone (18–34%), limestone (60–67%), and Indian sediment (6–15%) (Fig. 9b). A mixture with similar proportions of dolostone, limestone, and clastic sediments also explains the co-variation of Mg and O isotopes (Fig. 9c). Therefore, the variations of Mg, O, and Sr isotopic compositions can be best explained by mixing dolostone, limestone, and clastic sediments in the mantle source region of the Kuzigan and Zankan plutons.

The contamination by both limestone and dolostone indicates that the hybridized depth in the mantle is shallow because the stability of deeply recycled carbonates strongly depends on their depth in the mantle (Kushiro, 1975; Sato and Katsura, 2001; Dasgupta and Hirschmann, 2010). Therefore, the mantle source of the syenites and syenogranites in Kuzigan and Zankan areas had been hybridized at a depth shallower than 60 to 120 km, consistent with a previous study that suggested a <70 to 100 km metasomatized mantle source inferred from the metasomatic volatile phase relation (phlogopite and amphibole) (Jiang et al., 2012).

5.4. Implication for carbonate recycling during subduction of the Tethyan oceanic slabs

Pamir syntaxis is a complex subduction accretion system formed by northward subduction of the Tethyan ocean to Asia during Paleozoic to early Cenozoic. Particularly, huge amounts of carbonates were transported into the deep mantle along with the subduction and closure of the Neo-Tethys ocean. According to the carbon budget, a part of carbon was released to the surface by volcanic emission of CO₂, which was suggested to be responsible for the global warming during Cretaceous to early Cenozoic (Kerrick and Connolly, 2001; Kent and Muttoni, 2008). Another part of carbon was stored in carbonate minerals and recycled into the deep mantle. In this case, the recycling carbonates would be recorded in mantle-derived post-collisional magmatic rocks distributed in Tibet–Pamir region.

Ultrapotassic and potassic samples from the Kuzigan alkaline complex reveal that carbonates were involved into the upper mantle source based on their low $\delta^{26}$Mg isotopic compositions. Such a signature has also been observed in the Zankan syenites to the south in the Pamir region. Coincidentally, the Oligocene–Miocene (24 to 10 Ma) ultrapotassic volcanic rocks from the central and southern Lhasa subterrains also exhibit the similar low $\delta^{26}$Mg values, implying the carbonate contamination in the mantle underneath the Tibet plateau (Liu et al., 2015). It is reasonable to speculate that recycled carbonate might be broadly existent in the mantle sources of the Cenozoic potassic and ultrapotassic igneous rocks that are widely distributed in the Tibetan–Pamir Plateau. More studies are needed to constrain the spatial–temporal scale of carbonate metasomatism in the upper mantle underneath the Tibetan Plateau.

6. Conclusion

We report the Mg, O, and Sr isotopic compositions for the syenites and evolved syenogranites from the Kuzigan and Zankan plutons of the Pamir syntaxis in NW Xinjiang, China. The main conclusions are:

1. The alkaline syenites and syenogranites from the Kuzigan and Zankan regions have light Mg isotopic compositions with $\delta^{26}$Mg varying from −0.46 to −0.17‰. Syenites and syenogranites have similar Mg isotopic compositions, indicating limited Mg isotope fractionation during alkaline magma fractional crystallization.

2. The syenites display a negative correlation between Mg and O isotopic compositions, which suggest the involvement of recycled sedimentary carbonates in their mantle source.

3. The combined Mg–Sr–O Sr isotopic data could be used to identify the species of recycled carbonates and thus constrain the metasomatized mantle. The carbonated peridotite source for the Kuzigan and Zankan alkaline plutons could be mainly in mantle lithosphere (60 to 120 km).

4. In view of the tectonic setting of the Pamir syntaxis, the recycling of carbonate was likely related to subduction of the Tethyan oceanic slab during Mesozoic–Cenozoic.

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