Ultra-high Excess Argon in Kyanites: Implications for Ultra-high Pressure Metamorphism in Northeast Japan

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Abstract
A laser fusion Ar-Ar technique applied on single crystals of kyanite from river sands of the Kitakami Mountain region of northeast Japan yielded ages of up to 16 Ga, more than three times the age of the earth. Although the age values are geologically meaningless, the ultra-high excess argon in kyanites is unique and hitherto unreported. We interpret this to be an artifact of ultra-high argon pressure derived from radiogenic argon in potassium-rich phases such as phengites during the Barrovian type retrogression of the ultra-high pressure rocks in this region.

Key words: Ultra-high excess argon, kyanite, Barrovian, UHP rocks, Ar-Ar age.

Introduction
The Abukuma Mountains in northeast Japan, is a typical andalusite-sillimanite type metamorphic sequence (Miyashiro, 1958). However, this terrane has been under debate since long following some reports of kyanite - staurolite assemblages (Kano and Kuroda, 1968), which are indicative of Barrovian type metamorphism implying significantly different P/T conditions as compared with the andalusite-sillimanite type. Although in situ kyanite-bearing rocks are extremely rare in this region, kyanite and staurolite have been commonly recovered from river sands in the Abukuma and Kitakami mountains (Research Group of Abukuma Plateau, 1969; Kitakami River Sand Research Group, 1982).

In this study, we report the results from fusion Ar-Ar technique on single crystals of kyanite recovered from river sands in the Kitakami region. However, the kyanites yielded ages that are two to three times older than the age of the earth. We discuss the significance of the ultra-high excess argon in kyanites and its bearing on the Barrovian type retrogression of the ultra-high pressure rocks in the region.

Samples and Ar-Ar Analyses
The Kitakami Mountains are divided into the North and South Kitakami belts. The study area is located in the central part of the South Kitakami belt consisting of basement rocks, the Silurian-Early Cretaceous sedimentary sequences, and mafic to ultramafic rocks, intruded by Early Cretaceous Tono granitic rocks. The basement rocks comprise Paleozoic Hikami granites and Tsubonosawa metamorphic rocks, including the Motai and Unoki metamorphics, which have undergone partial thermal metamorphism through the intrusion of Cretaceous granitic rocks, making any precise dating difficult. The kyanite-bearing sites are mainly distributed in the southern part of the Tono mass where Carboniferous sedimentary sequences including the Tsubonosawa metamorphic rocks and the Hikami granitic rocks are distributed (Fig. 1). Kyanite here occurs in association with staurolite (Kitakami River Sand Research Group, 1982), suggesting that the host rocks had kyanite-staurolite assemblages of Barrovian type.

In the present study, kyanite was concentrated from the river sand at the K670 site in the Ohbata Village using heavy liquid technique and systematic acid treatment (mixture of H₂SO₄, HCl and HF, followed by HCl). Finally, the mineral was handpicked under a microscope. Figure 2 is a photomicrograph of the kyanite used in this study,
the chemical composition of which was confirmed to be nearly pure Al₂SiO₅ using electron microprobe techniques.

Ar-Ar analyses of the kyanite crystals were carried out using laser fusion technique. Each grain was placed in a 2 mm drill hole in an aluminum tray. Subsequently the tray was vacuum-sealed in a quartz tube. The samples were irradiated by neutrons in the core of 5 MW Research Reactor at Kyoto University (KUR) for 24 hours together with age standard grains (3gr hornblende; Roddick, 1983), and calcium (synthetic CaSi₂) and potassium (synthetic KAlSi₃O₈ glass) salts for Ca and K corrections. The fast neutron flux density is 3.9 x 10¹³ n/cm²/sec and is confirmed to be uniform in the dimension of the sample holder (16 x 15 mm) as little variation in J-values of the evenly spaced age standards was observed (Hyodo et al., 1999). Averaged J-values, potassium and calcium correction factors are J = 0.02034±0.00009, (40/39) K = 0.0186±0.0035, (36/37)Ca = 0.000304±0.000019 and (39/37)Ca = 0.00150±0.00008, respectively.

Each crystal was heated using a 5 W continuous argon ion laser. The extracted gas was purified with a SAES Zr-Al getter (St 101) kept at 400°C for 5 minutes. Argon isotopes were measured using the custom-made mass spectrometer with a relatively high resolution ([M/ΔM]>400), which allows separating hydrocarbon peaks except for mass 36 (Hyodo et al., 1994). Typical blanks of extraction lines are 5x10⁻¹⁴, 3x10⁻¹⁴, 3x10⁻¹⁴, 3x10⁻¹⁴ and 2 x 10⁻¹² ccSTP for ³⁶Ar, ³⁷Ar, ³⁸Ar, ³⁹Ar and ⁴⁰Ar, respectively. Results are shown in table 1. The ages are two to three times older than the age of the Earth.

Discussion

Ages older than the Earth’s age have been previously reported from diopsides in eclogite lens from gneiss and peridotite (4.7 to 8.1 Ga: K-Ar, McDougall and Green, 1964), diopsides in skarn from amphibolite (10 Ga: K-Ar, Hart and Dodd, 1962), ultramafic rocks in Kola Peninsula.
(8 Ga:Ar-Ar, Kaneoka, 1974) and in cubic diamonds from Zaire (6 Ga:K-Ar, Zashu et al., 1986; Ar-Ar, Ozima et al., 1989). One of the kyanite grains in this study gave an age of 16 Ga, which is the oldest age record so far (Fig. 3).

Obviously, these ages are geologically meaningless. Such values possibly result from the excess argon derived from various sources. The calculated potassium concentration from the 39Ar volumes of the kyanites are approximately one hundredth of the age standard, 3gr. Using the potassium concentration of 3gr given by Turner et al. (1971), the estimated potassium concentration in the kyanite is 13 ppm. Such low concentration is undetectable by electron microprobe techniques. Old ages can also result by leaching out potassium or as an artifact from calcium correction on 39Ar. However, this is unlikely from the following reasons. The hypothesis assumes only potassium to be leached out without the release of radiogenic 40Ar, which would remain at the ex-40K sites. In addition, original K concentration larger than 10 wt.% should be needed to explain the observed excess Ar concentration. Also, calcium correction was very little or none as only very small volume of 37Ar was observed. Therefore, we infer that excess 40Ar is the dominant factor, with only very little radiogenic component in the kyanite.

We calculated the concentration of 40Ar in each kyanite grain using the size measured under microscope, analytical data (Table 1), and the density (3.6 g/cm³). The excess argon contents ranged from 8.8 to 1700 x 10⁻⁶ ccSTP/g (Table 1). The sample Ky7 (11 Ga) has the highest concentration of 1.7 x 10⁻³ ccSTP/g, being close to that in Ky6 (29 Ga) and Ky7 (1.1) (Fig. 2).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>36Ar (10E-14cc STP)</th>
<th>37Ar (10E-14cc STP)</th>
<th>38Ar (10E-14cc STP)</th>
<th>39Ar (10E-14cc STP)</th>
<th>40Ar (10E-12cc STP)</th>
<th>Ar-Ar age (Ga)</th>
<th>Excess Argon 40 (10E-6cc STP/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ky6 (29)</td>
<td>3.6±1.1</td>
<td>0.9±1.2</td>
<td>3.5±1.0</td>
<td>6.9±1.5</td>
<td>246.7±1.0</td>
<td>7.7±0.4</td>
<td>8.8</td>
</tr>
<tr>
<td>Ky7 (1.1)</td>
<td>-</td>
<td>8.2±2.1</td>
<td>70.2±2.1</td>
<td>8.1±1.8</td>
<td>1904.9±6.4</td>
<td>11.1±0.4</td>
<td>1700</td>
</tr>
<tr>
<td>Ky8 (11)</td>
<td>-</td>
<td>0.4±1.3</td>
<td>3.9±1.1</td>
<td>5.7±2.3</td>
<td>11865±74</td>
<td>15.1±0.7</td>
<td>1100</td>
</tr>
<tr>
<td>Ky9 (11)</td>
<td>-</td>
<td>0.2±1.2</td>
<td>3.2±0.9</td>
<td>10.5±2.1</td>
<td>1227±36</td>
<td>9.9±0.4</td>
<td>11</td>
</tr>
<tr>
<td>Ky11 (17)</td>
<td>-</td>
<td>1.4±0.8</td>
<td>2.5±2.1</td>
<td>10540±30</td>
<td>16.3±1.5</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>Ky13 (18)</td>
<td>7.6±9.2</td>
<td>-</td>
<td>2.1±0.8</td>
<td>2.4±1.5</td>
<td>554.6±1.3</td>
<td>11.1±1.1</td>
<td>31</td>
</tr>
</tbody>
</table>

Numerals in parenthesis of sample number show sample weight in µg (see text).

Fig. 2. Photomicrographs of representative kyanite crystals recovered from river sand.
beryl in pegmatites as reported by Aldrich and Nier (1948), by far the highest record of excess argon (2.5 x 10^-3 ccSTP/g). No age was available for the beryl because potassium concentration was not measured.

It should be noted that the diopsides, ultramafic rocks, diamonds and kyanites that yielded ages older than the Earth's age are markedly low in potassium and could be strongly affected by the excess argon to yield the extremely older age. The samples, Ky 7 and Ky 8 having excess argon of the order of 10^-3 ccSTP/g, indicate that they might have formed in ultra-high argon partial pressure environment.

We suggest that such high argon pressures might have resulted from the low argon retentivity of some potassium bearing phases in the host rocks.

Excess argon has also been reported from phengites in ultra-high pressure (UHP) and associated high pressure (HP) metamorphic rocks in Dora Maira massif, Italy (Arnaud and Kelley, 1995; Scaillet, 1996), Sesia-Lanzo zone, Italy (Ruffet et al., 1997; Inger et al., 1996), Su-Lu and DaiBie area, China (Li et al., 1994), Kaghan Valley, Pakistan (Tonarini et al., 1993), Tavsanli, Turkey (Sherlock and Arnaud, 1999) and Betic zone, Spain (de Jong et al., 2001). The UHP eclogitic rocks occur normally as blocks or lenses in the pelitic schists and gneisses. Recently, Katayama et al. (2001) reported diamond and coesite inclusions within zircons in the pelitic schists and gneisses associated with the eclogite from the Kokchetav massif, northern Kazakhstan. Nakamura and Hirajima (2000) and Nakamura (2002) proposed an adiabatic exhumation of the UHP rocks to explain the formation of the gneisses at medium to low pressure and high temperatures. These studies suggest that Barrovian-type metamorphic rocks can be generated through the retrogression of UHP rocks. Kyanite coexisting with jadeite in such UHP rocks would decompose to paragonite during adiabatic exhumation. The mineral would thus form under Barrovian-type P/T conditions in the crust, acquiring excess argon during recrystallization. We postulate that the kyanites reported in this study might have recrystallized in their host rocks under ultra-high argon pressure derived from radiogenic argon in potassium-rich phases such as phengites during the Barrovian type retrogression of UHP rocks. Kyanite with excess argon of 1.7 x 10^-3 ccSTP/g has the potential for extremely high argon retentivity and may provide important clues on the tectono-metamorphic history of the UHP rocks. Our interpretations are limited by the fact that the kyanites reported in this study were collected from river sediments and not directly from host rocks.

Future studies on kyanites from host rocks would further resolve this issue.

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DISCUSSION

Feldspar Alteration and Diagenetic Characteristics of the Parsora Sandstones, Son Basin, India – Comment*

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In response to the paper ‘Feldspar Alteration and Diagenetic Characteristics of the Parsora Sandstones, Son Basin, India’ by Babar Ali Shah and D.N. Bandopadhyay (Gondwana Newsletter, 24, Gondwana Research, v. 8, pp. 258-265), I am making a few comments, asking for certain clarifications and expressing my views on a few observations made in the paper. My objective is to generate a debate that will help all of us to understand the diagenetic history of Parsora sandstones from a wider perspective.

According to the authors, Parsora sandstones are mineralogically immature, feldspar-rich arkose. They observed that the sandstones contain 70 percent quartz

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