

## Low-pressure and low-temperature K-bearing kosmochloric diopside from the Osayama serpentinite mélange, SW Japan

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### ABSTRACT

Kosmochloric diopside with high K content up to 0.56 wt% (0.026 K atom per formula unit) was discovered from the Osayama serpentinite mélange in the Chugoku Mountains, SW Japan. K-bearing clinopyroxene fills microcracks (5–150  $\mu\text{m}$  in wide) together with uvarovite within albite vein of a tremolite rock. Compositions of analyzed clinopyroxene consist mainly of kosmochlor + augite (92–98 mol%;  $\text{Ko}_{19-38}\text{Aug}_{56-76}$ ) components and minor amounts of jadeite (0–6 mol%), aegirine (0–5 mol%), Ca-Tschermak (0–3 mol%), and K-kosmochlor (0–2 mol%). Although the K content in clinopyroxene is also variable and heterogeneous even in a single vein, clinopyroxene with higher K content occurs in Ko-rich part. Higher magnification secondary electron images confirmed that exsolution and inclusion are essentially absent in the analyzed clinopyroxenes. The good negative correlation between  $\text{Cr} + \text{Na} + \text{K}$  and  $\text{Ca} + \text{Mg} + \text{Fe}^{2+}$  indicates the Cr incorporation into the octahedral site. Furthermore, K correlates with Na and Cr, indicating a simultaneous enrichment of K for Na and Cr during pyroxene growth. Textural relations, and parageneses and compositions of minerals suggest that the K-Cpx precipitated together with uvarovite in brittle microcracks directly from a Ca- and Cr-rich hydrothermal fluid at approximately  $P < 0.3$  GPa and  $T < 400$  °C. Although it has been experimentally concluded that only ultrahigh- $P$  ( $>4$  GPa) environment permits to host relatively large  $\text{K}^+$  cation into the clinopyroxene structure, our finding indicates that the incorporation of K into the kosmochlor–diopside series solid solution with at least 0.2 Cr cation p.f.u. is possible even at low  $P$  conditions.

### INTRODUCTION

“K-jadeite ( $\text{KAlSi}_2\text{O}_6$ )” and “K-kosmochlor ( $\text{KCrSi}_2\text{O}_6$ )” are fictive but realistic components of the clinopyroxene solid solution; these were extrapolated from both natural and synthetic K-bearing clinopyroxenes (K-Cpx) at ultrahigh-pressure (UHP)  $> 4$  GPa (e.g., Harlow 1997; Harlow and Davies 2004). At least two types of K-Cpx-hosted lithologies have been reported: (1) mantle-derived xenoliths in kimberlite–lamproite pipes and intermediate alkaline intrusions (Reid et al. 1976; Bishop et al. 1978; Jaques et al. 1990; Harlow and Veblen 1991; Ghorbani and Middlemost 2000), and (2) regional UHP metamorphic rocks (e.g., Sobolev and Shatsky 1990; Zhang et al. 1997; Katayama et al. 2000; Okamoto et al. 2000; Bindi et al. 2002). These UHP occurrences were verified by recent experiments that considerable amounts of K could be accommodated in the clinopyroxene structure under the mantle condition of  $P > 3$ –17 GPa and  $T > 900$ –1500 °C; the solubility of K increases with increasing pressure (e.g., Harlow 1997; Luth 1997; Okamoto and Maruyama 1998; Harlow 1999; Perchuk et al. 2002; Safonov et al. 2003) and decreases with temperature (Okamoto and Maruyama 1998). Obviously both experiment and natural parageneses indicate that UHP is necessary to incorporate K into clinopyroxene. In this paper, however, we present the first report of relatively high K (up to 0.56 wt%  $\text{K}_2\text{O}$ ) content in natural chromian clinopyroxene that formed in low  $P$ - $T$  environment.

### GEOLOGIC OUTLINE

K-Cpx was found in microcracks within albite vein of a tremolite rock from the Osayama serpentinite mélange (OSM), SW Japan; the OSM is a serpentinite-matrix mélange with Paleozoic blueschist blocks (Tsuji-mori 1997, 1998; Tsujimori and Itaya 1999; Tsujimori and Liou 2005) (Fig. 1). In the OSM, two types of tremolite-rich rock occur: high- $P$  tremolite schist of peridotite-origin (type-I), and low- $P$  tremolite-rich rind at the boundaries between blueschist blocks and serpentinite (type-II). Type-I schist contains relict chromian spinel that replaced by blueschist-facies chromian minerals such as omphacite, pumpellyite and phengite; Tsujimori and Liou (2004) described chromian omphacite (jadeite [ $\text{Jd}$ ]<sub>23-41</sub> kosmochlor [ $\text{Ko}$ ]<sub>5-20</sub> augite [ $\text{Aug}$ ]<sub>47-61</sub> aegirine [ $\text{Ae}$ ]<sub><7</sub>) with chromian diopside lamellae ( $\text{Jd}_{4-18}\text{Ko}_{1-14}\text{Aug}_{73-94}\text{Ae}_{<3}$ ) from a variety of type-I schists. On the other hand, type-II tremolite rind is relatively massive and does not contain blueschist-facies minerals. Instead randomly oriented diopside occurs especially in the thermal aureole of late Cretaceous granitic intrusions. Sakamoto and Takasu (1996) described chromian pyroxenes ( $\text{Jd}_{<3}\text{Ko}_{0.1-54}\text{Aug}_{45-98}\text{Ae}_{0.5-7}$ ) of the kosmochlor–diopside series with a radial habit; this may be a variety of type-II rocks. The investigated sample is a variety of the type-II rock.

### PETROGRAPHY AND SEM OBSERVATIONS

The investigated sample consists mostly of tremolite ( $>95\%$ ) with a small amount of diopside. The sample was cataclastic,

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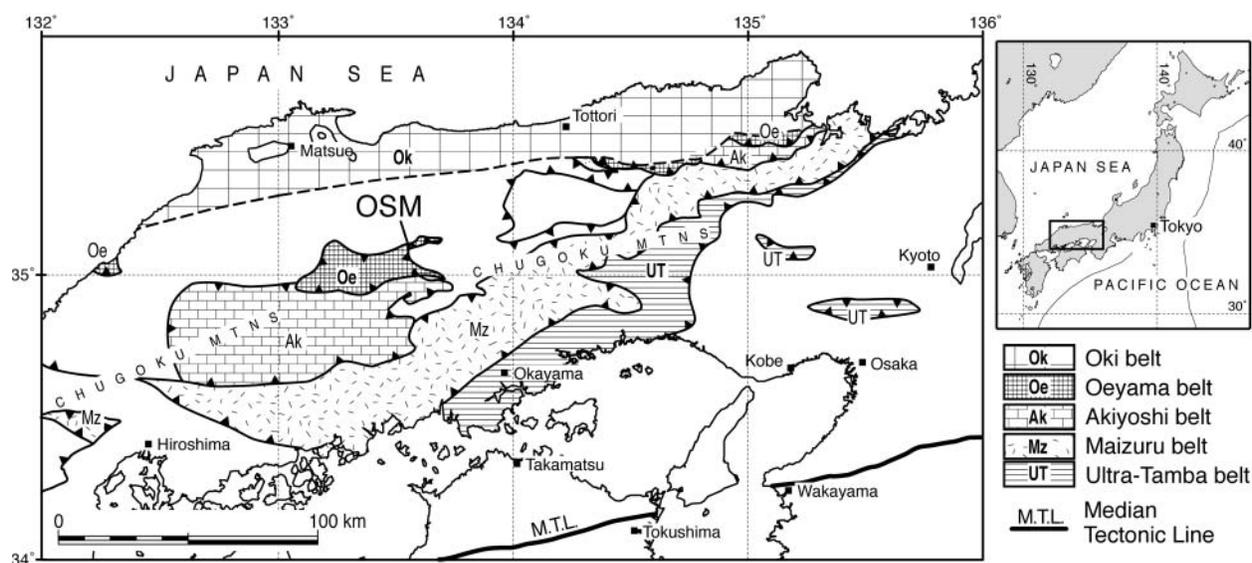


FIGURE 1. Simplified map of the Chugoku Mountains, showing various petro- and tectonic units and the sampling locality in the Oosayama serpentinite mélangé (OSM) (modified after Tsujimori and Liou 2004).

and exhibits multiple brittle fractures with hydrothermal veins of various parageneses. Coarse-grained albite (1–3 mm in size) aggregates fill brittle fractures (<8 mm in wide) to form albite veins that were cross-cut by uvarovite veins of 5 to 150  $\mu\text{m}$  wide. K-Cpx is closely associated with uvarovite in microcracks; most occur as irregular-shape aggregates of tiny anhedral crystals (<30  $\mu\text{m}$ ) with striking emerald-green pleochroism, and fill interstices of euhedral to subhedral uvarovite. The micro-size veins were petrographically investigated using an electron microprobe, and a scanning electron microscope (SEM). X-ray images were obtained using a JEOL JXA-8900R at Okayama University of Science with an accelerating voltage of 15 kV. Higher magnification secondary electron images were obtained using an FEI XL30 Sirion SEM at Stanford University with an accelerating voltage of 5 kV. X-ray images demonstrated a biminerale mineral association of uvarovite and clinopyroxene, and confirmed the chemical heterogeneity of vein-filled clinopyroxenes (Fig. 2). Moreover, higher magnification SEM observations corroborated the textural homogeneity that exsolution and inclusion are essentially absent in the investigated clinopyroxenes (Fig. 3).

### Mineral chemistry

Electron microprobe analysis was carried out with a JEOL JXA-8900R at Okayama University of Science. Quantitative analyses were performed with 15 kV accelerating voltage, 12 nA beam current and 3  $\mu\text{m}$  beam size. Natural and synthetic silicates and oxides were used as standards for calibration. The CITZAF method was employed for matrix corrections. Natural sanidine was used for K standard; the detection limit of  $\text{K}_2\text{O}$  is  $\sim 0.01$  wt%. For the clinopyroxene analysis, the presence of K was indicated by the wavelength dispersive X-ray scans using PET (pentaerythritol) diffraction crystal; K-Cpx shows a significant K ( $K\alpha$ ) peak (Fig. 4). Representative analyses of K-Cpx and other minerals are listed in Table 1.

### K-bearing clinopyroxenes

The analyzed K-Cpx contains 6.5–13.2 wt%  $\text{Cr}_2\text{O}_3$ , 3.1–5.7 wt%  $\text{Na}_2\text{O}$ , 0.8–1.7 wt%  $\text{Al}_2\text{O}_3$ , and 1.2–4.1 wt% FeO. The K-Cpx in a single vein has heterogeneous composition and lacks systematic chemical zoning. The maximum K content reaches up to 0.56 wt%  $\text{K}_2\text{O}$ ; the average of 68 analyses is 0.18 wt%  $\text{K}_2\text{O}$ . Although the K content in clinopyroxene is variable and heterogeneous even in a single vein, clinopyroxene with higher K content occurs in Ko-rich part. The  $X_{\text{Mg}}$  [=  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  atomic ratio] and  $X_{\text{Cr}}$  [=  $\text{Cr}/(\text{Cr} + \text{Al})$  atomic ratio] range from 0.82 to 1 and 0.79 to 0.91, respectively. The good negative correlation between  $\text{Cr} + \text{Na} + \text{K}$  and  $\text{Ca} + \text{Mg} + \text{Fe}^{2+}$  of the analyzed K-Cpx indicates that a substitution,  $(\text{Na}, \text{K})_{\text{M1}}\text{Cr}_{\text{M2}} \leftrightarrow \text{Ca}_{\text{M1}}(\text{Mg}, \text{Fe}^{2+})_{\text{M2}}$ , is a dominant for the Cr incorporation into the octahedral site (Fig. 5). As shown in Figure 6, moreover, K correlates with Na and Cr, indicating a simultaneous enrichment of K for Na and Cr during pyroxene growth.

The clinopyroxene end-members were calculated following the technique given in Harlow (1999; personal comm. 2004). In the investigated sample, K is accommodated in the clinopyroxene in structure as  $\text{KCrSi}_2\text{O}_6$  (KKo, K-kosmochlor) component. The analyzed K-Cpx is composed principally of solid solutions lying in the Ko–Di series (Ko + Aug = 92–98%); major variations are along the Aug–Ko join with Aug ranging from 56 to 76 mol%, and Ko from 19 to 38 mol% (Fig. 7). Minor components include Jd < 6%, Ae < 5%, CaTs [Ca-Tschemack] < 3%, and KKo < 3%.

### Other minerals

K-free and less chromian clinopyroxene in the tremolite-rich matrix adjacent to the albite vein has a composition of Aug = 90–97%, Ko = 0–7% and Jd < 3% with  $X_{\text{Mg}} = 0.73$ –0.97 (Fig. 7). Uvarovite has a composition of Uvr = 69–71%, Grs = 17–22%, and Adr 7–11%, and contains up to 0.5 wt%  $\text{TiO}_2$ . Tremolite in

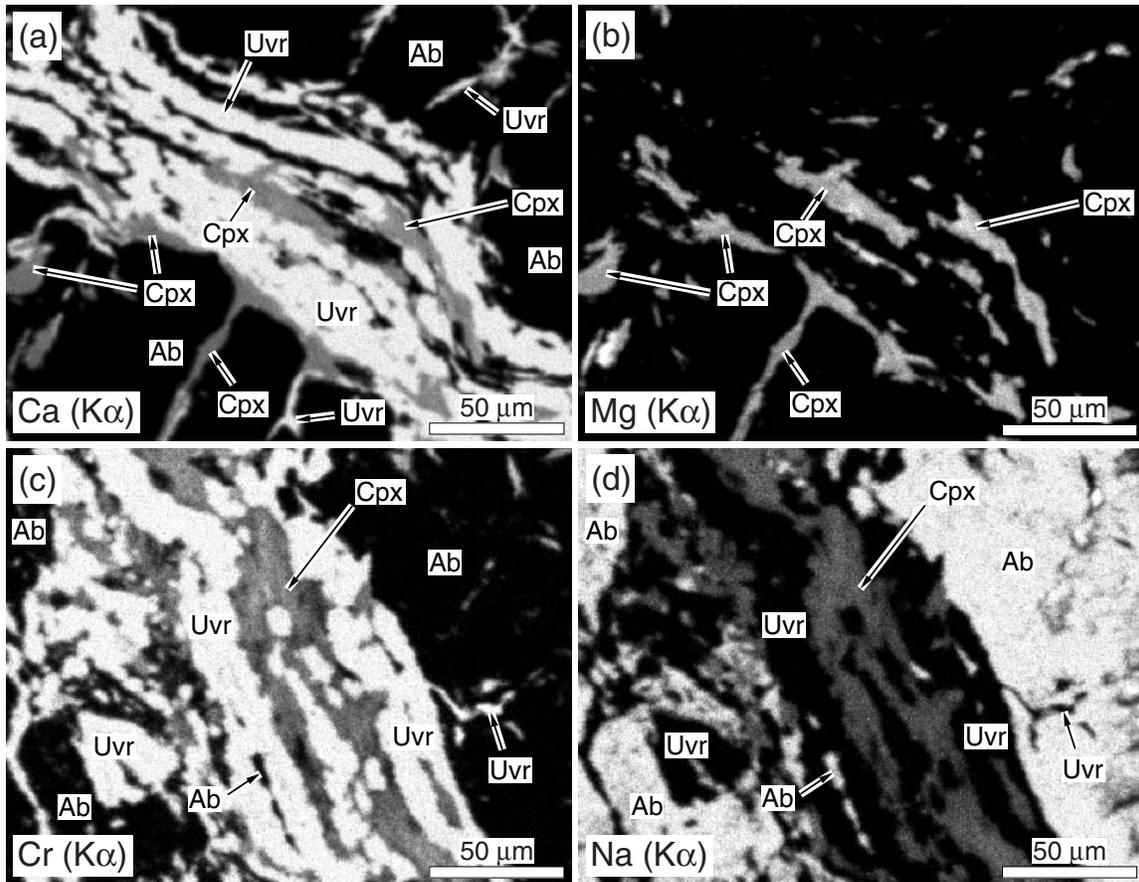


FIGURE 2. X-ray images showing occurrences and microtextures of the investigated clinopyroxene. (a) Ca ( $K\alpha$ ) image of K-bearing Cpx uvarovite vein. (b) Mg ( $K\alpha$ ) image of a. (c) Cr ( $K\alpha$ ) of K-bearing Cpx uvarovite vein. (d) Na ( $K\alpha$ ) of c.

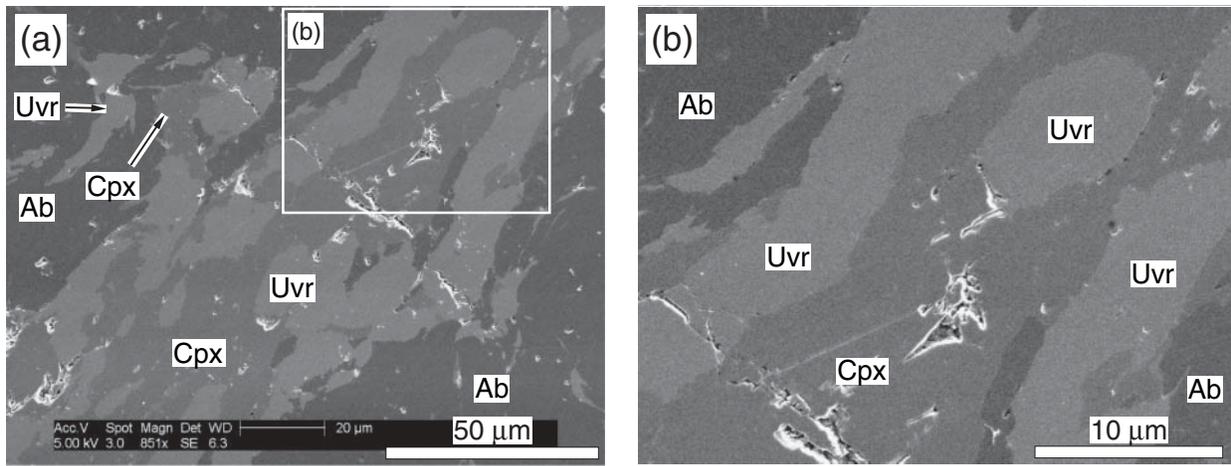


FIGURE 3. High-resolution secondary electron images showing occurrences of the investigated clinopyroxene. (a) Higher magnification image of K-bearing Cpx uvarovite vein. (b) Enlarged image of a part of a.

TABLE 1. Representative analyses of K-bearing Cpx and other minerals

	K-bearing clinopyroxene (Vein)					Uvarovite (Vein)		Host Rock Tremolite		Host Rock Clinopyroxene	
	1	2	3	4	5	1	2	1	2	1	2
SiO <sub>2</sub>	53.94	52.76	53.46	54.24	53.58	36.75	36.63	57.41	57.18	54.60	54.42
TiO <sub>2</sub>	0.13	0.12	0.11	0.14	0.12	1.43	0.66	0.00	0.09	0.19	0.01
Al <sub>2</sub> O <sub>3</sub>	1.06	1.40	1.30	1.33	1.11	4.16	4.45	0.06	0.16	0.60	0.72
Cr <sub>2</sub> O <sub>3</sub>	11.35	11.65	11.53	8.15	8.07	21.63	21.65	0.00	0.17	1.75	0.88
FeO*	3.01	3.52	3.01	2.85	3.16	2.18	2.45	3.22	3.67	4.49	2.66
MnO	0.15	0.19	0.13	0.15	0.13	0.16	0.15	0.07	0.18	0.21	0.21
MgO	9.58	9.25	9.42	11.55	11.01	0.09	0.11	22.22	21.57	14.05	15.94
CaO	15.56	15.35	15.48	17.84	18.04	34.26	34.23	13.04	12.80	23.24	24.45
Na <sub>2</sub> O	4.91	4.87	5.01	3.83	4.06	0.06	0.06	0.17	0.36	1.32	0.91
K <sub>2</sub> O	0.56	0.54	0.36	0.25	0.07	0.00	0.00	0.02	0.15	0.00	0.00
Total	100.26	99.65	99.82	100.33	99.35	100.72	100.37	96.21	96.33	100.45	100.19
O=	6	6	6	6	6	12	12	6	6	6	6
Si	1.996	1.969	1.987	1.991	1.988	2.976	2.978	7.994	7.994	2.001	1.977
Ti	0.00425	0.003	0.003	0.004	0.003	0.087	0.040	0.000	0.009	0.005	0.000
Al	0.046	0.062	0.057	0.058	0.049	0.397	0.426	0.009	0.026	0.026	0.031
Cr	0.332	0.344	0.339	0.237	0.237	1.385	1.391	0.000	0.018	0.051	0.025
Fe <sup>3+</sup>	0.001	0.028	0.020	0.000	0.027	0.132	0.149	0.062	0.000	0.005	0.053
Fe <sup>2+</sup>	0.092	0.082	0.092	0.088	0.071			0.312	0.429	0.132	0.028
Mn	0.005	0.006	0.004	0.005	0.004	0.010	0.010	0.008	0.021	0.007	0.006
Mg	0.529	0.515	0.522	0.632	0.609	0.010	0.012	4.612	4.495	0.767	0.863
Ca	0.617	0.614	0.616	0.702	0.717	2.973	2.982	1.945	1.917	0.912	0.952
Na	0.352	0.352	0.361	0.273	0.292	0.009	0.009	0.045	0.096	0.094	0.064
K	0.026	0.026	0.017	0.012	0.003	0.000	0.000	0.002	0.026	0.000	0.000
Total	4.000	4.000	4.000	4.000	4.000	7.983	8.001	14.994	15.035	4.000	4.000
X <sub>Mg</sub>	0.85	0.86	0.85	0.88	0.90			0.94	0.91	0.85	0.97
Ko	31	32	32	23	23					5	3
K-Ko	3	3	2	1	0.3						
Aug	62	59	61	70	71					91	93

Notes: FeO\* = total Fe as FeO. X<sub>Mg</sub> = Mg/(Mg + Fe<sup>2+</sup>). The Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio and end-members of Cpxs were calculated based on cation charge balance (Harlow 1999).

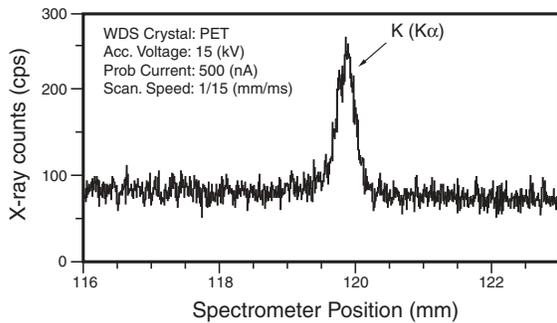


FIGURE 4. X-ray count chart showing K (K $\alpha$ ) peak of the investigated clinopyroxene.

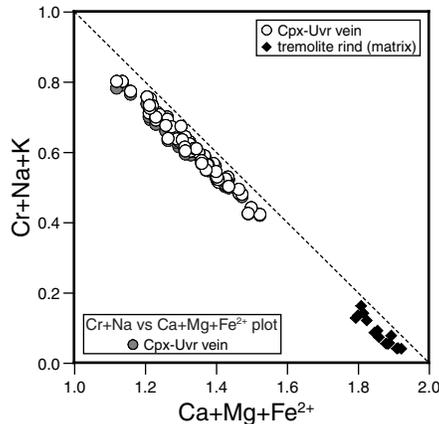


FIGURE 5. Compositional plots of the analysed clinopyroxenes on the Cr + Na + K vs. Ca + Mg + Fe<sup>2+</sup> diagram.

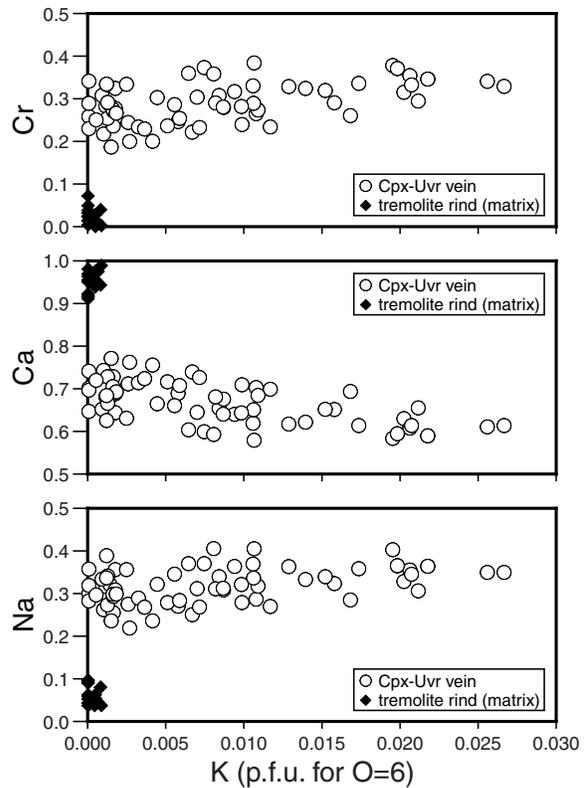


FIGURE 6. Various plots of clinopyroxene K cation (p.f.u. for O = 6).

tremolite-rich matrix contains 0.04–0.16 wt% K<sub>2</sub>O, 0.16–0.38 wt% Na<sub>2</sub>O and 0–0.39 wt% Cr<sub>2</sub>O<sub>3</sub>; the  $X_{Mg}$  ranges from 0.91 to 0.93.

#### *P-T* condition for the formation of k-bearing clinopyroxenes

As described above, the investigated K-Cpx fills the albite veins along microcracks of type II tremolite rinds. This texture clearly indicates that the precipitation of uvarovite and K-Cpx from a hydrothermal fluid postdated the formation of albite veins. The local mineralization in the microcrack may be coeval with the formation of albite vein at *P-T* condition within the albite stability, at least below the brittle-ductile transformation *T* of albite (ca. 450 °C) (Tullis and Yund 1991). Furthermore, very low Jd (<6 mol%) and CaTs (<3 mol%) components in the K-Cpx confirm such low-*P* and -*T* condition.

In the OSM, blocks and veins of low-*P* rodingites and albitite occur together with high-*P* blueschist blocks (Tsuji-mori 1998); the assemblage of diopsidic pyroxene + grossular-rich garnet (rare uvarovite-rich) is common in these low-*P* metasomatic rocks. Moreover, some authigenic uvarovite and aragonite veins occur in serpentinite. These parageneses indicate that the K-Cpx crystallized together with uvarovite from a Ca- and Cr-rich K-bearing hydrothermal fluid at *P* < 0.3 GPa and *T* < 400 °C. The Cr-rich hydrothermal fluid should have been incorporated from serpentinite; the heterogeneity of Cr content in K-Cpx may be related to a heterogeneous composition of local fluid. The fluid-rock interaction and latest brittle deformation may have been induced by abundant late Cretaceous granitic activities in the Chugoku Mountains.

## DISCUSSIONS

#### Comparisons with the other K-bearing clinopyroxenes at UHP

Until now, natural K-Cpx with up to 3.1 and 2.3 wt% K<sub>2</sub>O content has been reported from UHP metamorphic rocks from the Kokchetav Massif, northern Kazakhstan (Bindi et al. 2002) and mantle xenoliths in hawaiite from the Warrumbungle Volcano, Southeastern Australia (Ghorbani and Middlemost 2000) respectively, whereas other reported natural K-Cpx crystals contain as much as 0.2–1.7 wt% K<sub>2</sub>O (e.g., Harlow and Veblen 1991). Moreover, the incorporation of K at the peak condition has also been inferred from the occurrence of exsolution lamellae of K-feldspar in clinopyroxenes of diamondiferous UHP rocks (e.g., Reid et al. 1976; Sobolev and Shatsky 1990; Zhang et al. 1997). In the electron-microprobe quantitative analysis, significant K contents may have sometimes been detected from clinopyroxene as contamination with inclusions of K-bearing materials (Perchuk et al. 2002). For instance, Mellini and Cundari (1989) described K-bearing aegirine phenocryst (up to 0.11 wt% K<sub>2</sub>O) in leucitite from Australia, but their TEM observations confirmed K-bearing glassy lamellae infiltrating aegirine. In our sample, however, K-bearing glass is not expected, because it was formed at low-*T* subsolidus condition. Moreover, submicrometer-scale inclusions or lamellae were not found through higher magnification SEM observations as described above.

As comparing with other K-Cpx in literatures, the K content up to 0.56 wt% K<sub>2</sub>O in the investigated K-Cpx from the Chugoku Mountains has similar K content to that from UHP lithologies. In spite of large ionic radius of K<sup>+</sup> (1.51 Å; Shannon 1976) to enter

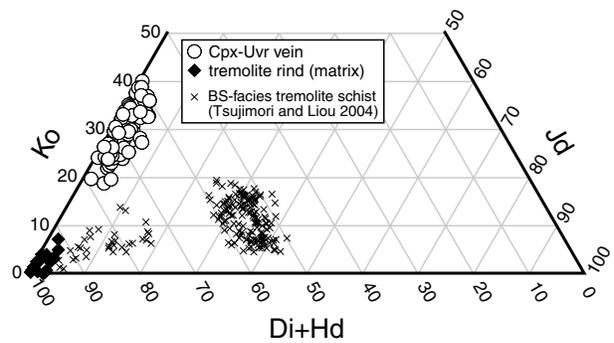


FIGURE 7. Compositional plots of the analysed clinopyroxenes on the Ko-(Di + Hd)-Jd ternary diagram. For the comparison, compositions of blueschist-facies chromian omphacite–diopside from the OSM (Tsuji-mori and Liou 2004) are also illustrated.

the M2 site of Cpx at normal crustal conditions, K can be accommodated in the Cpx structure at UHP (> 4 GPa) environments (e.g., Harlow and Davies 2004). The polyhedral compressibility of Na and K are relatively large in comparison with Ca, hence Na and K decrease in size with increasing pressure; K substitutes as a scheme of Ca<sub>M2</sub>(Mg, Fe<sup>2+</sup>)<sub>M1</sub> ↔ K<sub>M2</sub>(Al, Cr)<sub>M1</sub> (Harlow 1997). This explains the restricted occurrences of natural and synthetic K-Cpx at UHP conditions and the dependence on *P* of K content of clinopyroxene. However, our investigated K-Cpx formed at low-*P* within the stability of albite. Thus, we emphasized that UHP is not essential conditions for the incorporation of K into the kosmochloric diopside.

#### A compositional constraint on K in clinopyroxene at low-pressure and -temperature

The special characteristic of the investigated K-Cpx is the significant Ko component (21–39 mol%) in the diopsidic solid solution. Harlow and Veblen (1991) and Harlow (1997) suggested that diopsidic solid solution with a unit-cell volume ( $V_c$ ) of ~439 Å<sup>3</sup> is a better host for K than omphacite ( $V_c$  = ~425 Å<sup>3</sup>), jadeite ( $V_c$  = ~401 Å<sup>3</sup>) and kosmochlor ( $V_c$  = ~419 Å<sup>3</sup>). Furthermore, they also inferred that the incorporation of Cr<sup>3+</sup> might expand the M2 site for occupancy by K; the charge balancing of K<sup>+</sup> by substitution of Cr<sup>3+</sup> is more effective than Al<sup>3+</sup>.

In general, diopsidic pyroxenes are stable at low *P-T* condition (e.g., Maruyama and Liou 1985; Banno 1998), and contain negligible K<sub>2</sub>O content below the detection limit of electron-microprobe analyses. However, our low *P-T* kosmochloric diopside contains measurable K<sub>2</sub>O content. This suggests that the incorporation of Cr plays an important role for K solubility in the diopsidic solid solution as suggested by Harlow (1997).

Compositions of the investigated K-Cpx are plotted together with UHP chromian K-Cpx of Harlow and Veblen (1991) and Harlow (1997) in the Cr vs. K diagram (Fig. 8). The K/Cr ratio of the investigated K-Cpx is remarkably smaller than that of the UHP chromian K-Cpx, while they show similar positive correlations between K and Cr. These relationships lead us to delineate possible qualitative isopleths on the Cr-K plot of Figure 7. Alternatively, the possible isopleths suggest that at least 0.2 Cr cation p.f.u. is needed to accommodate K into diopsidic solid solution

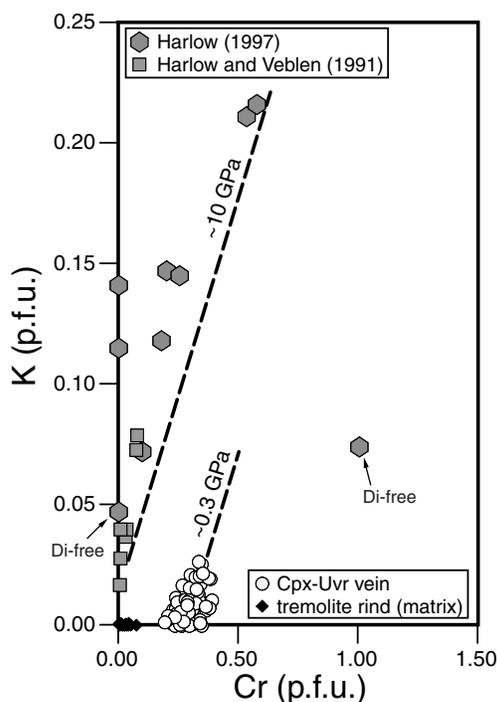


FIGURE 8. Plots of clinopyroxene cations (p.f.u. for O = 6) of the investigated clinopyroxene on the Cr vs. K diagram.

at low-*P* environments, whereas K can be accommodated in Cr-free diopsidic pyroxenes at UHP.

Apparently, natural kosmochloric diopside occurs in both UHP (e.g., Sobolev et al. 1975; Harlow and Veblen 1991; Liu et al. 1998) and low *P-T* rocks (Sakamoto and Takasu 1996; Reznitskii 1999; Secco et al. 2002; this study). A complete miscibility along the Ko–Di (Aug) join has been recently confirmed by Secco et al. (2002). In fact, a continuous solid solution between these end-members has long been demonstrated by Yoder and Kullerud (1971) at *P* = 0.2 GPa and *T* = 500–700 °C. The kosmochloric diopside formed at low *P-T* environments may have a potential to carry considerable amount of K.

Nevertheless, the mechanism to accommodate K at low-*P* is still unclear. Recently, Sakamoto et al. (2003) suggested the incommensurate structure from the Ko–Di series clinopyroxene (Sakamoto and Takasu 1996) from the OSM. Although they did not determine K content, it may be possible that this crystallographic structure of the intermediate composition between Ko–Di assists K incorporation at low *P-T*.

#### ACKNOWLEDGMENTS

This research was supported financially in part by JSPS Research Fellowship for Research Abroad of the first author. Preparation of this manuscript was supported by NSF EAR-0003355. We thank Toru Takeshita for his useful comments on brittle deformation of albite. We are grateful to R.E. Jones for technical assistance in SEM observations. This manuscript has been critically reviewed by W.G. Ernst. The authors acknowledge careful review by G.E. Harlow and R.W. Luth, and editorial assistance by E.D. Ghent.

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MANUSCRIPT RECEIVED JUNE 22, 2004

MANUSCRIPT ACCEPTED MAY 2, 2005

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