Extremely Fe-rich metamorphic sekaninaite in a sillimanite-grade schist clast from the Middle Jurassic conglomerate, Hida Mountains, Japan

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Abstract Extremely Fe-rich metamorphic sekaninaite (Fe^{2+}-dominant analogue of cordierite) with 0.16-0.21 $Mg/(Mg+Fe^{2+})$ ratio was found in a cobble of garnet-sillimanite schist from Middle Jurassic conglomerate (Tetri Group) in the Hida Mountains, Japan. Sekaninaite occurs as reaction corona replacing relict porphyroblastic almandine-rich garnet; it contains 0.17-0.35 wt.% Na_2O. Microtextural relationship defines the primary stage (M_1: Grt + Bt + Sil) and the sekaninaite-forming stage (M_2: Sek + Bt + Sil). The sekaninaite-bearing phase equilibria constrains a qualitative metamorphic condition of T = 610-790˚C and P = 60-320 MPa for the M_2, and suggests a decompressional cooling path form the M_1 (P = c. 330 MPa at nominal T = 740˚C). Fe-rich sekaninaite composition may reflect unusually low $Mg/(Mg+Fe^{2+})$ ratio (0.14) of bulk-rock composition.

Keywords: sekaninaite, Fe-cordierite, metapelite, sillimanite grade, Tetri Group, Hida Mountains

INTRODUCTION

The cordierite group mineral is common in low-pressure (LP) granulite and migmatite terranes. Most metamorphic cordierite group minerals are Mg-rich with more than 0.5 X_{Mg} [=$Mg/(Mg+Fe^{2+})$ ratio] (e.g., Leake, 1960; Bhattacharya et al., 1988). On the other hand, Fe^{2+}-rich cordierite, sekaninaite, has very restricted occurrences as a primary phase in felsic igneous rock and migmatite (e.g. Stanke and Miskovsky, 1964; Cerny et al., 1997; Hiroi et al. 2001; Rapela et al. 2002). Although sekaninaite-forming reaction in the system KFASH (K_2O-FeO-Al_2O_3-SiO_2-H_2O) has been experimentally determined or thermodynamically calculated (e.g., Richardson, 1968; Mukhopadhyay and Holdaway 1994), the results indicate that this phase is stable as a subsolidus phase in high-T metamorphic rocks. However, metamorphic sekaninaite has scarcely been described in natural parageneses (e.g., Spear and Chaney, 1989).

Extremely Fe-rich metamorphic sekaninaite (0.16-0.21 X_{Mg}) was recently found in a sillimanite-grade metapelite clast from Middle Jurassic conglomerate unit at Hida Mountains, Japan. Parageneses and compositions of sekaninaite and its associated minerals from this high-grade metapelite are investigated. Such unusual occurrence was interpreted in terms of bulk composition and P-T conditions. Mineral abbreviations are after Kretz (1983) except for sekaninaite (Sek) throughout this paper.

SAMPLE DESCRIPTION AND PETROGRAPHY

Sekaninaite-bearing schist sample (TD-KZ4/6) was collected as a well-rounded cobble (10 × 8 cm) in a Middle Jurassic conglomerate bed of the Tetori Group at Kuzuryu area, central Japan (Fig. 1). The Tetori Group unconformably overlies Hida Triassic Barrovian-type gneiss-schist terrane in the Hida Mountains. Clasts of the conglomerate bed consist mainly of quartzite, granite, marble, metapelite and sandstones (e.g., Yamada et al., 1989); Tsujimori (1995) described a staurolite-sillimanite schist cobble possibly derived from the Hida terrane.

The sample is a medium-grained and well-foliated metapelite; no anatextic texture such as leucozome was observed. It consists mainly of fibrous sillimanite, quartz, garnet, and sekaninaite with minor amount of biotite, plagioclase (An_{6-8}) and ilmenite, and trace K-feldspar, monazite, and apatite. Sekaninaite occurs as reaction coronas around relict garnet porphyroblasts (Fig. 2a, 2b and 2c) and a rare matrix phase. The corona is composed mainly of mosaic aggregates of sekaninaite with tiny inclusions of biotite, quartz, ilmenite, apatite and rare monazite. The original size of garnet porphyroblast may reach up to 7 mm in diameter, judged from the shape of reaction corona. Relict garnet contains inclusions of tiny ilmenite, quartz and apatite. Microtextural relationship indicates two stages of metamorphic recrystallization: the M_1 stage assemblage includes garnet porphyroblast setting in a foliated matrix of Sil + Bt (M_1) +Pl + Qtz and the M_2 assemblage consists of Sek + Bt (M_2) + Qtz. Sekaninaite was formed by the breakdown of garnet and is the most characteristic phase for the M_2 event. Secondary chlorite and sericite locally replace sekaninaite.

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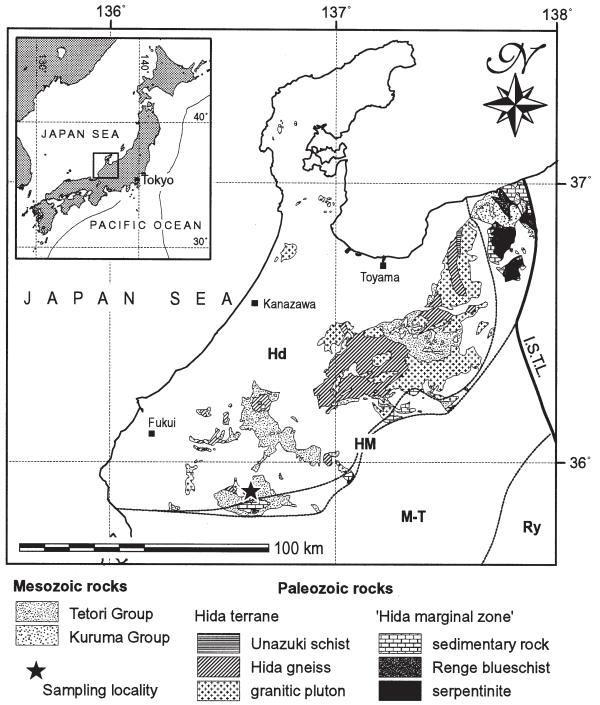

Fig. 1. Distribution map of pre-Cretaceous rocks in the Hida Mountains, Japan (after Tsujimori, 2002) and the locality of the Kuzuryu area. Hd = Hida terrane; HM = Hida marginal zone; M-T = Mino-Tamba accretionary complex; Ry = Ryoke LP metamorphic belt; I.S.T.L. = Itoigawa-Shizuoka Tectonic Line.

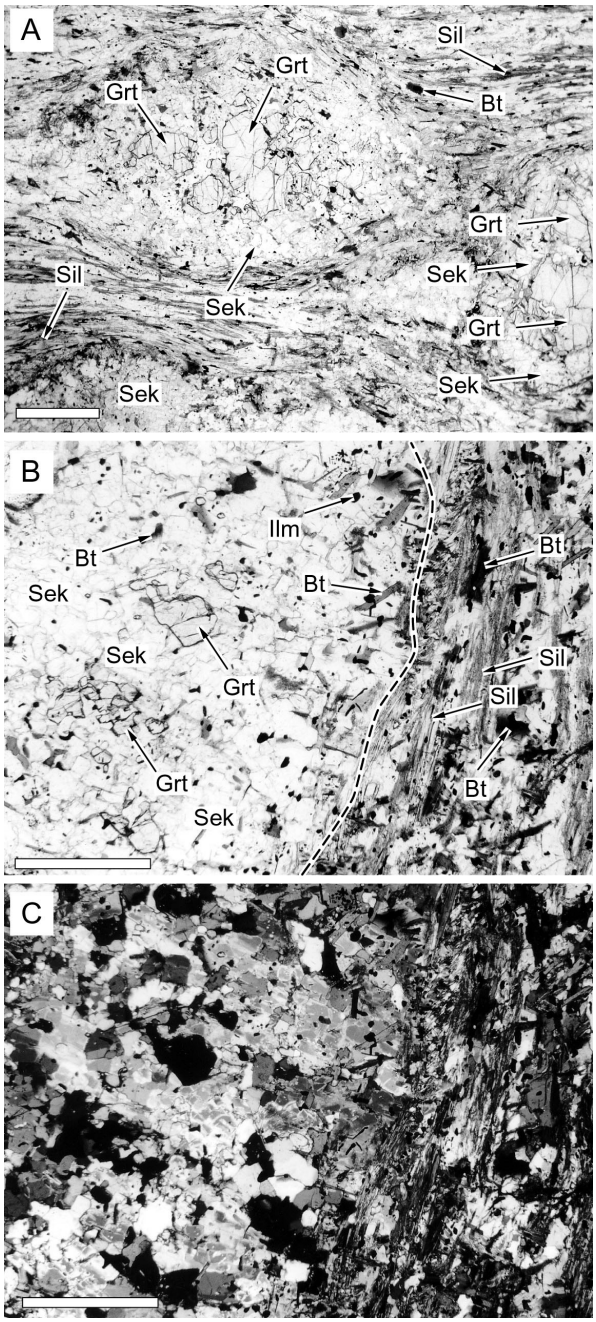

Fig. 2. Photomicrograph showing microtexture of sekaninaite in garnet-sillimanite schist. (A) Plane-polarizer view showing sekaninaite replacing porphyroblastic garnet; preferred orientation of fibrous sillimanite defines a foliation. Scale bar represents 1 mm. (B) Enlarged image of coronitic sekanianite; sekaninaite contains biotite and quartz. Scale bar represents 0.5 mm. (C) Cross-polarizer view of (B).

WULK-ROCK CHEMISTRY

Bulk-rock composition of the sekaninaite-bearing sample was analyzed by a Rigaku System 3270 X-ray fluorescence spectrometer with Rh tube at Kanazawa University; the operating conditions were 50 kV accelerating voltage and 20 mA beam current. The result is given in Table 1. It is characterized by high in Al_2O_3 (26.0 wt.%), SiO_2 (57.2 wt.%) and total iron oxide as FeO (12.4 wt.%), but low in K_2O, (0.7 wt.%), MgO (1.2 wt.%), CaO (1.2 wt.%) and Na_2O (2.4 wt.%), with 27 mol% normative corundum, 38 mol% quartz and 21 mol% normative albite; the Mg/(Mg+Fe) and $Al_2O_3/(CaO + Na_2O + K_2O)$ molar ratios are 0.14 and 3.55, respectively. This highly peraluminous and iron-rich features suggest that the protolith has originated as bauxitic supracrustal sediment.

MINERAL CHEMISTRY

Electron microprobe analysis and X-ray element mapping were carried out with a JEOL JXA-8800R at Kanazawa University. The quantitative analyses of rock-forming minerals were performed with 15 kV accelerating voltage, 12 nA beam current and 3-5 μm beam size. Natural and synthetic silicates and oxides were used as standards. The ZAF method (oxide basis) was employed for matrix corrections. Representative analyses of sekaninaite and other minerals are listed in Table 2; compositions of these minerals and rock are plotted in an AFM diagram of Figure 3.

Sekaninaite. Sekaninaite contains essentially 16.9-18.2 wt% FeO as total Fe, 30.9-32.0 wt% Al_2O_3, 46.2-47.3 wt% SiO_2 with less than 2.6 wt % MgO and 0.35 wt.% Na_2O (0.04-0.07 Na p.f.u. for O=18); the analysed sekaninaite shows a negative correlation of Si against Na + Al, indicating a substitutions Si in tetrahedral site ⇔Na in channel site plus Al in tetrahedral site (Wolfsdorff and Schreyer 1992). The X_{Mg} of sekaninaite varies from 0.16 to 0.21; no systematic chem-

ical difference is observed in spite of their occurrences. Anhydous total of analyzed oxides add to only 98.0-99.2 wt.% suggesting e appreciable content of volatile molecules.

Garnet (relict). Relict garnet is enriched in almandine component with minor pyrope, spessartine and grossular components ($Prp_{2-4}Alm_{92-93}Sps_{2-5}Grs_{<1}$). The X_{Mg} varies from 0.02 to 0.03. Core of relict garnet has slightly high Mn content.

Biotite. The matrix M_1 biotite contains 1.1-1.4 wt.% TiO_2 whereas M_2 biotite inclusions in coronitic sekaninaite contains 2.4-3.2 wt.% TiO_2.The X_{Mg} of the M_1 biotite and M_2 biotite are 0.15-0.16 and 0.10-0.13, respectively.

Other minerals. Sillimanite contains 0.1-0.2 wt.% Fe_2O_3. Ilmenite in coronitic sekaninaite contains up to 2.0 wt.% MnO.

P-T CONDITION FOR THE SEKANINAITE-FORMATION

In the studied sample, the coronitic replacement of sekaninaite after porphyroblastic garnet can be expressed by one reaction in the KFASH system such as

3 Sek = 2 Alm + 4 Sil + 5 Qtz ····· (1)

The end-member reaction in Mg-free system has been experimentally determined and thermodynamically calculated (e.g. Richardson, 1968; Mukhopadhyay and Holdaway, 1994), and constrains a maximum P < 200 MPa at T = 700-750 ˚C (Mukhopadhyay and Holdaway 1987). In the KFASH system with excess Qtz + Kfs + H_2O, the *P-T* limit of the M_2 Sek + Bt + Sil assemblage is defined by the following reactions together with reaction (1) (Fig. 5):

Ms + Qtz = Kfs + Sil + H_2O ····· (2);

And = Sill ····· (3); and

Bt (Ann) + 6 Qtz = 3 Opx (Fs) + 2 Kfs + 2 H_2O ····· (4).

Moreover, no textural evidence of anatexis suggests that the vapor-saturated melting reaction in the KASH system

Kfs + Sil + Qtz + H_2O = liquid (Spear et al., 1999) ····· (5)

constrains the high-T limit of the M_2 assemblage. The *P-T* condition for the M_2 was calculated using the software BAYES (Chatterjee et al., 1998) with activities of minerals 0.66 for sekaninaite, 0.75 for garnet and 0.18 for biotite (annite) and 1.0 for the other phases to be T = 610-790 ˚C and P = 60-320 MPa (Fig. 5). The activity models for such estimates are based on Holland and Powell (1998). The moderate Na contents (up to 0.06 p.f.u.) of sekaninaite further support the estimated T condition (Mireald, 1986; Kalt et al., 1998).

On the other hand, the *P-T* condition of the M_1 assemblage may be constrained by the GASP geobarometer reaction, 2 Sill + Grs + Qtz = 3 An. it gives an approximate P = c. 330 MPa at nominal T = 740 ˚C. This suggests that the metamorphic evolution from M_1 to M_2 is characterized by a decompressional cooling.

COMPARISON WITH THE OTHER METAMORPHIC SEKANINAITE

Few metamorphic sekaninaites with higher X_{Mg} have been docu-

Table 1. Bulk-rock composition of sekaninaite-bearing schist.

Sample	TD-KZ4/6
SiO_2	52.46
TiO_2	1.62
Al_2O_3	25.97
FeO*	12.35
MnO	0.20
MgO	1.16
CaO	1.18
Na_2O	2.14
K_2O	1.52
P_2O_5	0.04
Total	98.64

FeO* = total Fe as FeO.

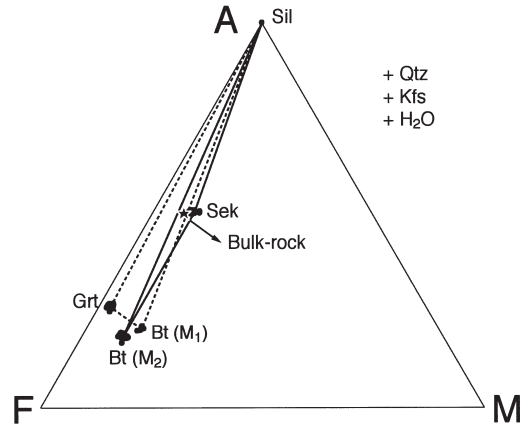

Fig. 3. AFM diagram projected from K-feldspar showing analyzed mineral compositions and a bulk-rock composition.

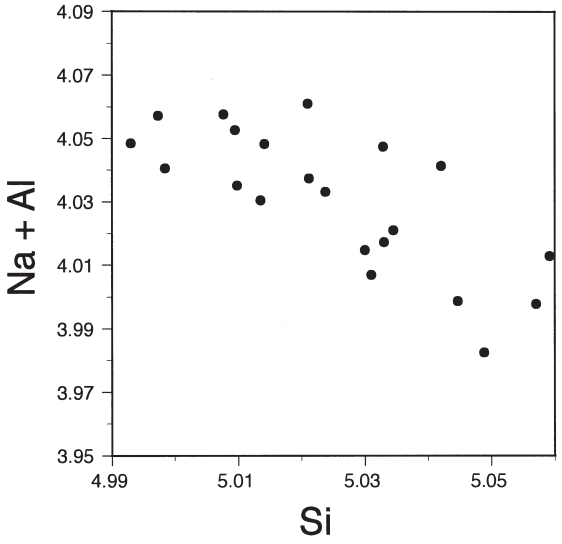

Fig. 4. Si versus (Na + Al) diagram showing the Si ⇔ Na + Al substitution of analyzed sekaninaite. The amounts of Si, Na and Al are calculated based on structural formulae units.

Table 2. Representative electron-microprobe analyses of sekaninaite, garnet, biotite, and plagioclase.

	Sekaninaite			Garnet		Biotite		Plagioclase	
			average (N=21)			M_1	M_2		
SiO_2	46.69	46.96	46.84	37.15	36.74	33.57	33.78	65.51	66.27
TiO_2	0.00	0.05	0.02	0.06	0.03	1.22	2.91	0.01	0.04
Al_2O_3	31.49	31.65	31.49	20.14	20.95	21.61	20.15	20.89	20.80
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.06	0.00
FeO*	17.75	17.75	17.55	41.06	40.43	28.04	27.87	1.96	0.26
MnO	0.21	0.19	0.20	1.05	1.62	0.06	0.00	0.00	0.05
MgO	2.02	2.30	2.22	0.97	0.60	2.70	1.95	0.19	0.00
CaO	0.07	0.00	0.03	0.22	0.23	0.00	0.00	1.52	1.73
Na_2O	0.22	0.24	0.24	0.03	0.00	0.18	0.20	10.42	10.86
K_2O	0.00	0.00	0.00	0.00	0.00	9.25	9.31	0.13	0.05
Total	98.46	99.13	98.59	100.67	100.61	96.62	96.22	100.70	100.06
O=	18	18	18	12	12	22	22	8	8
Si	5.021	5.014	5.025	3.035	3.002	5.246	5.310	2.874	2.911
Ti	0.000	0.004	0.001	0.003	0.002	0.144	0.344	0.000	0.001
Al	3.991	3.982	3.981	1.938	2.017	3.980	3.732	1.080	1.077
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.002	0.000
Fe^{3+}								0.065	0.009
Fe^{2+}	1.596	1.585	1.574	2.805	2.762	3.665	3.664		
Mn	0.019	0.017	0.019	0.073	0.112	0.008	0.000	0.000	0.002
Mg	0.324	0.366	0.354	0.118	0.073	0.629	0.457	0.012	0.000
Ca	0.008	0.000	0.004	0.019	0.020	0.000	0.000	0.072	0.081
Na	0.046	0.049	0.050	0.004	0.001	0.054	0.059	0.886	0.925
K	0.000	0.000	0.000	0.000	0.000	1.844	1.866	0.007	0.003
Total	11.006	11.016	11.008	7.995	7.988	15.569	15.440	4.999	5.009
X_{Mg}	0.17	0.19	0.18	0.03	0.01	0.15	0.11		

FeO* = total Fe as FeO. X_{Mg} = Mg/(Mg+Fe^{2+})

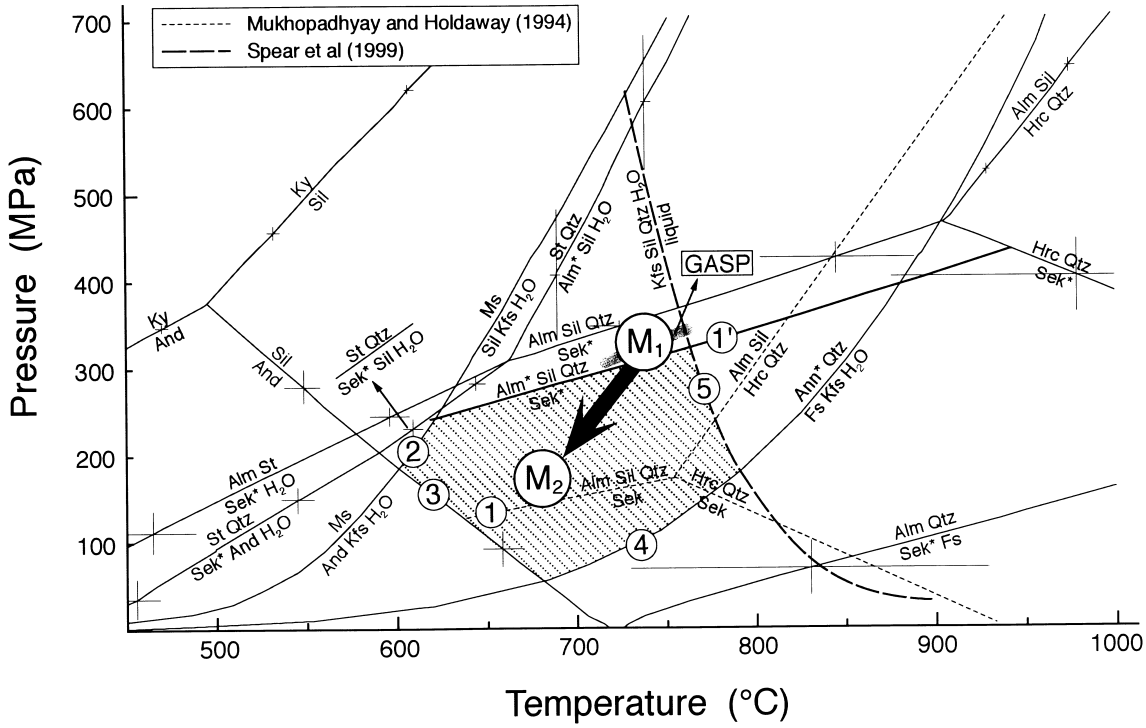

Fig. 5. *P-T* diagram showing selected phase relationships and a qualitative *P-T* estimations. All reactions of solid lines are calculated by the software BAYES (Chatterjee et al., 1998); crossed bars represent 1 σ error of the calculation. Mineral abbreviations with '*' represent minerals with fixed activities as < 1.0 (see text). The melting reaction (5) is after Spear et al. (1999). Dashed lines involving reaction (1) are after Mukhopadhyay and Holdaway (1994). The reactions curves of (1') represents an isopleths of the reactions (1).

mented. For examples, those with $X_{Mg} > 0.28$ in metapelite of a contact aureole from the Island of Kos (Greece) coexist with biotite, andalusite, garnet, hercynite and rare sillimanite (Kalt et al., 1998); most of them were formed at the andalusite-stability field. Relict chloritoid is preserved in some sekaninaites of this locality according to a chloritoid-consuming reaction: Cld = Crd + Hrc + H_2O; the *P-T* condition was estimated to be $P < 400$ MPa at $T = 510$-750 ˚C. Metamorphic sekaninaites with $X_{Mg} > 0.40$ in pelitic granulite from the Nain complex, Labrador have been described by Berg (1977). They coexists with garnet and sillimanite or orthopyroxene; $P = 370$-660 MPa at $T < 915$ ˚C was estimated. The characteristics in these two cases are that the constituent minerals coexisting with sekaninaite are characterized by very low X_{Mg}. This indicates that the X_{Mg} of sekaninaite is not only attributed to Fe-Mg partitioning during continuous reaction but also strongly depends on Fe-rich bulk-rock composition.

The investigated sekaninaite from Japan is characterized by extremely low X_{Mg} (0.16-0.21). This may reflect unusually Fe-rich and very low X_{Mg} (0.14) for bulk rock composition. Although metamorphic sekaninaite is less common in the natural parageneses, it may appear stably at LP condition but in wide *T* range from the andalusite field to high above a granitic water-saturated solidus in the sillimanite field. However, the sekaninaite stability overlaps in the anatexitic conditions of LP metapelites. At $P <$ c. 400 MPa of the sillimanite field, a continuous dehydration melting reaction, Crd (Sek) + Bt = Grt + Sil + liquid, may occurs in the KFMASH (M = MgO) or NKFASH (N = Na_2O) systems (e.g. Brown, 1998; Spear et al., 1999). As the melting reaction has a negative slop, sekaninaite-consuming dehydration melting will occur with prograde evolution of LP pelitic rocks; the reaction shifts to lower *T* and *P* sides with decreasing bulk rock X_{Mg}. In the prograde LP metamorphic terranes and aureole, the sekaninaite-consuming melting may cause the rare occurrence of natural-metamorphic sekaninaite, even if the bulk-rock compositions to form sekaninaite are satisfied.

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