Pinkish colored epidotes found in a geothermal exploration well NB-1, Noboribetsu, Hokkaido

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Occurrence and mineralogical properties of pinkish colored epidotes that were found in core samples from a geothermal exploration well NB-1, Noboribetsu, Hokkaido, Japan are described together with estimating the formation conditions. The minerals occurred mainly as vein- and druse-fillings in volcaniclastic rocks of the Miocene Osarugawa Formation. They coexisted with brownish chlorites, K-feldspar, illite, and quartz, and associated with minor hematite, titanite, and/or apatite. The minerals were produced by local K-alteration that overprinted early-formed regional propylitization associated with ordinary greenish epidotes and chlorites. The cell parameters of pinkish epidote were: $a = 8.884(6)$, $b = 5.614(1)$, $c = 10.149(7)$ Å, $\beta = 115.5(8)°$, and $V = 456.9(4)$ Å$^3$. The $\text{Ca}_2\text{Mn}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$ contents of the pinkish epidotes were generally less than 2.4 mol%, while the $\text{Ca}_2\text{Fe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$ contents attained 28 mol%. It is considered that the low Mn contents and relatively low Fe contents resulted in giving the characteristic pinkish to pale yellow colors for epidote. Associated brownish chlorites were characterized by low total Fe and relatively high Fe$^{3+}$ contents. Their formation temperatures were estimated to be $230-300 \degree$C, using semi-empirical chlorite geothermometers. These data indicate that pinkish epidotes coexisted with brownish chlorites formed under oxidative conditions and probably low Fe contents in hydrothermal fluids.

Keywords: Pinkish epidote, Fe-poor chlorite, Geothermal field, Hydrothermal alteration

INTRODUCTION

Epidote-group minerals occur in a variety of geological environments such as low to high $P/T$ metamorphism, magmatism, and hydrothermal alteration (e.g., Deer et al., 1986; Liesbacher and Franz, 2004). According to the nomenclature system proposed by Armbruster et al. (2006), clinozoisite, epidote, and piemontite belong to the clinozoisite-subgroup, and the simplified structure formula is described by $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{12}(\text{OH})$, $\text{Ca}_2\text{Al}_2\text{Fe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$, and $\text{Ca}_2\text{Al}_2\text{Mn}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$, respectively. The manganian endmember, piemontite, is characterized by a deep red color. The color depends on the Mn content, and epidote or clinozoisite with low Mn contents often exhibits reddish colors ranging from red to yellow (Deer et al., 1986; Bonazzi and Menchetti, 2004). Piemontite is usually documented from regional low to medium grade metamorphic rocks and metamorphosed rocks originated from Mn-rich sediments and ore deposits. It is known that the formation of piemontite favors oxidative conditions in regional metamorphism (e.g., Keskinen and Liou, 1979; Kawachi et al., 1983; Bonazzi and Menchetti, 2004). Despite being scarce, the occurrences of reddish epidotes have been described in hydrothermally altered andesites and their volcanic sediments (e.g., Takeshita and Matsumoto, 1979; Takeshita et al., 1989) and in veinlets in pelitic schist (Shingu et al., 1990). Taylor and Baer (1973) reported the occurrence of reddish epidote with low Mn-contents from hydrothermal explosion breccias in Archean rocks, Newfoundland. Because of their scarcity, however, the formation conditions of reddish epidotes of hydrothermal process origin are still poorly understood. The present authors found pinkish colored epidotes in cores from a geothermal exploration well NB-1, Noboribetsu, Hokkaido. In this article the occurrence, chemical composition, and unit-cell parameters of the mineral are described comparing with the chemical compositions of associated chlorites formed under oxidative conditions in hydrothermal system.
GEOLOGICAL SETTING AND ALTERATION

Noboribetsu area, Hokkaido is one of active geothermal fields in Japan. Many exploration wells were drilled around this area by NEDO (NEDO, 1983, 1991) as shown in Figure 1. Among them, Hole NB–1 was drilled to a depth of about 1000 m in the Karurusu Spa area which is characterized by a subsurface depression structure like a caldera (Fig. 2). According to NEDO (1991), the depression structure is filled with Quaternary andesitic volcanics, named the Kuttara Volcanics and the Karurusu volcanic and detritus deposits, in the intervals from the surface to 680 m in depth. The Kuttara Volcanics to the depth of 212 m is locally intercalated with the Noboribetsu lake deposits and the Tachibana-ko lavas.

Underlying the Quaternary volcanics are the Osarugawa Formation of Miocene age, putting an unconformity between the two. The Orofure-toge Formation of Miocene age was unclear in NB–1. The Osarugawa Formation appears to the bottom of NB–1. It comprises mainly volcanic breccias to tuff breccias with angular to subangular andesitic rocks. Pre–Tertiary basement rocks, named the Ohmagarisawa Formation, were not encountered through NB–1, though the presence was recognized in adjacent holes such as NB–5 and NB–6 (Fig. 2). The Ohmagarisa Formation consists mainly of sandstones, tuffs, tuff breccias, and andesitic lavas or dikes in this area. The present subsurface temperature is about 100 °C at the bottom of NB–1 (Figs. 2 and 3). Comparison with fluid inclusion data in NB–1 (NEDO, 1991) indicates that hydrothermal activity in NB–1 has been ceased.

Based on preliminary studies of cores from NB–1 together with other wells from the Noboribetsu and Iburi areas, hydrothermal alteration encountered through NB–1 is classified into four types of alteration taken place at different stages (Fig. 3). The Kuttara Volcanics contained unaltered glasses in the upper parts and altered to halloysite and smectite in the lower parts. Acid alteration with kaolinite, alunite, and pyrite developed in the Karurusu Volcanics near the bottom of depression structure. These alteration minerals are products of recent hydrothermal activities. The Osarugawa Formation was subjected to regional propylitization which is characterized by the mineral assemblages of albite, greenish epidote, greenish chlorite, quartz, calcite, and illite (Meyer and Hemley, 1967). Actinolite occurred near the bottom of hole. The deepest parts of propylitization were characterized by the appearance of biotite as seen in T–1 and NB–4 (Fig. 3).
The propylitic mineral assemblages are products of early hydrothermal alteration because laumontite veins cross-cut the biotite zone in NB-4. A granitic intrusive mass was encountered in the bottom of T-1 (Fig. 2). NEDO (1991) reported a K-Ar age of 39.3 ± 1.7 Ma for the granite, the age which seems to be too old to affect alteration of the Miocene Osarugawa Formation. So far, the heat sources or hydrothermal activities responsible for the early propylitization are unspecified yet. The propylitic alteration was overprinted by hydrothermal alteration of later stages, one is what is characterized by the formation of Ca-zeolites such as laumontite and wairakite; the other is K-alteration diagnostic of the occurrence of K-feldspar and illite in addition to pinkish epidotes of interest here. The K-alteration appears to postdate the hydrothermal alteration formed Ca-zeolites. In addition, acid alteration associated with pyrophyllite and rectorite (regularly interstratified illite-smectite mineral) as well as kaolinite was observed through NB-5 and NB-3 (Fig. 3).

SAMPLES STUDIED AND METHODS

Seven core samples of Hole NB-1, two pinkish epidote-bearing rocks at 837.4 and 897.7 m depth and five adjacent propylite rocks at 792.7, 808.9, 880.5, 888.2, and 996.5 m depth, were examined in detail in the present study. The whole rock mineralogy was firstly determined by X-ray powder diffraction (XRD: Rigaku RAD I-B, 40 kV, 25 mA, graphite-monochromatized Cu Kα radiation) and optical microscopy using thin sections. Clay fractions (<2 µm) that were separated from rocks by ultrasonic vibration and centrifugation were provided to examine the nature of interlayering, the polytypic structure, and the \( d_{001} \) values. Cell parameters of pinkish epidote were determined by XRD with silicon standard using a software of CellCalc (Miura, 2003) on the basis of indexing by Shingu et al. (1990).

Chemical analysis of secondary minerals in polished thin sections was carried out using scanning electron microscopy with an energy-dispersive type spectrometer (SEM-EDX: JEOL JSM-5600 equipped with an Oxford Link ISIS-300). The chemical composition was determined using the conditions: an accelerating voltage of 15 kV, a beam current of 0.8 nA, an analyzed area of about 5 × 6 µm², and a counting time of 100 sec. EDX data were reduced by a ZAF correction scheme. The standard materials included quartz (Si), corundum (Al), periclase (Mg), synthetic fayalite (Fe), rhodonite (Mn), anatase (Ti), wollastonite (Ca), albite (Na), and adularia (K). All Fe and Mn in epidote were assumed to be Fe³⁺ and Mn³⁺ respectively. Those in chlorite were tentatively regarded as divalent cations. Titanium was assumed to be Ti⁴⁺ for all the minerals.
RESULTS AND DISCUSSION

Occurrence and mineral assemblages

Mineral assemblages of 7 samples studied are listed in Table 1. Pinkish epidotes, observed in two core samples at 837.4 and 897.7 m depth of NB–1, occurred as fillings of veins and druses in rocks (Fig. 4a). In the sample at 897.7 m, fine-grained pinkish epidotes also were pervasive in the matrix of rock. The color ranged pale yellow to pinkish under plane-polarized light, and that of an epidote grain observed changed from pink in the core to colorless to pale yellow in the rim. They sometimes exhibited a sector zoning (Fig. 4b) and oscillatory–like zoning (Figs. 4c and 4d). In contrast, epidotes replacing plagioclase and filling veins and druses in propylitically
altered rocks showed ordinary greenish to yellowish colors (Figs. 4e and 4f). It is noted that pinkish epidote coexists with brownish chlorite, K-feldspar, illite, and quartz (Figs. 4b, 5c, and 5d). In a vein with pinkish epidote in the sample at 837.4 m, greenish chlorite appears to be crosscut by brownish chlorite (Fig. 5d). The sample at 897.7 m was wholly silicified, and original albite was decomposed by the overprinting K-alteration which formed pinkish epidotes and brownish chlorites. The K-alteration additionally affected adjacent propylite rocks to form apatite and/or titanite (e.g., samples at 792.7, 808.9, and 888.2 m, Table 1). Epidotes with ordinary greenish color in propylites usually coexisted with greenish chlorites, which is typical in the sample at 792.7 m. But in such rocks chlorites were surrounded by dark brown rims and/or partially replaced by brown clays (Figs. 5a and 5b). The minerals

Figure 4. Photos showing the modes of occurrence of pinkish and greenish epidotes in rock and thin sections. (a) core sample with pinkish epidote veins from 897.7 m, (b) a pinkish epidote grain [epidote (P)] showing a sector zoning in vein under plane polarized light (837.4 m), K-spar, K-feldspar; (c) a pinkish epidote grain showing an oscillatory-like zoning under plane polarized light (897.7 m), (d) photomicrograph of (c) under crossed polarized light, (e) and (f) greenish epidotes [epidote (G)] under plane polarized light (888.2 m). Color version is available online from http://doi.org/10.2465/jmps.161229.
of rims and central brown clays were illite by EDX analysis as described below. Brownish chlorite in the sample at 837.4 m contained titanite as well as pyrite grains (Fig. 5c). The pyrite grains were rimed by fine–grained epidotes, suggesting that pyrite may be metastable. The modes of occurrence observed indicate that later K–alteration influenced rocks at 800–900 m depth to a considerable extent. The stage of associated carbonate mineral formation remains unsolved at moment.

Optical properties and cell parameters of pinkish epidote

The pinkish epidotes had somewhat lower birefringences than the epidotes and were optically negative; their 2V values were significantly large, qualitatively >70°. Thus this sample may be called pinkish epidote, not pinkish clinozoisite or piemontite, following the published studies cited in Deer et al. (1986) and Franz and Liebscher (2004).

Using the sample at 897.7 m depth, cell parameters determined by XRD were: \(a = 8.884(6), b = 5.614(1), c = 10.149(7) \text{ Å}, \beta = 115.5(8)^\circ\), and \(V = 456.9(4) \text{ Å}^3\). These values are similar to those of low Mn–bearing clinozoisite–epidote solid solution series reported in the literatures (e.g., Deer et al., 1986; Franz and Liebscher, 2004) and of pink–colored epidote reported by Shingu et al. (1990) as well.

Chemical compositions of epidotes and associated minerals

Chemical compositions of epidotes are summarized in Table 2. Magnesium was tentatively cast to the octahedral
cations of epidote structure. Strontium and REE were not detected. Assuming that total number of oxygen = 12.5 and all Mn = Mn$^{3+}$, the total numbers of positive charges ($\alpha$) were close to an ideal value of 25 (24.99 < $\alpha$ < 25.01). It is reasonable to assume that the presence of Mn$^{2+}$ is negligible and Mn$^{3+}$ substitutes for Al or Fe$^{3+}$ in the M sites of epidote structure.

The chemical compositions of epidotes are plotted in a Ca$_2$Al$_3$Si$_3$O$_{12}$O(OH)-Ca$_2$Fe$_3$Si$_3$O$_{12}$O(OH)-Ca$_2$Mn$_3$Si$_3$O$_{12}$O(OH) triangle diagram (Fig. 6). The contents of Ca$_2$Mn$_3$Si$_3$O$_{12}$O(OH) component were wholly less than 2.4 mol%. Greenish epidotes contained 20-38 mol% of Ca$_2$Fe$_3$Si$_3$O$_{12}$O(OH) component. In the two zoned epidote grains analyzed, the core was enriched in Fe relative to the rim; the color changed from greenish yellow in the core to colorless in the rim. In contrast, the Ca$_2$Fe$_3$Si$_3$O$_{12}$O(OH) component in pinkish epidotes was less than those in the epidotes, mostly <28 mol%. The contents of Ca$_2$Mn$_3$Si$_3$O$_{12}$O(OH) component changed from nil to 2 mol% in oscillatory-zoned grains concomitant with an increase in the Ca$_2$Fe$_3$Si$_3$O$_{12}$O(OH) component from 22 to 28 mol%. The compositions were clearly distinguished between pinkish and pale-yellowish parts in a sector zoned grain (Fig. 6). Fine-grained epidotes rimming pyrites (837.4-m sample) have similar compositions to the epidotes.

Chemical compositions of chlorites associated with pinkish and greenish epidotes are summarized in Table 3. The Mn contents were generally less than 0.08 atoms per formula unit in both greenish and brownish chlorites. The compositions are plotted in an Al(total)-(Fe + Mn)-Mg triangle diagram (Fig. 7). The Mg/(Fe + Mn + Mg) ratios were quite distinct between greenish and brownish chlorites. In the sample at 808.9 m, there were two populations of compositions; relatively Fe-rich greenish chlorites were from fillings of early veins and relatively Fe-poor ones were partially replaced by illite (Figs. 5a and 5b). In the sample at 837.4 m, greenish chlorites in veins were rich in Fe, while brownish chlorites were poor in Fe (Fig. 5d). The occurrences of greenish and brownish chlorites indicate that early-formed greenish chlorites in propylite altered to brownish chlorites during later stage K-alteration. In the sample at 897.7 m, the Fe content in brownish chlorite increased as a function of distance from the proximal part of pinkish epidote grain to the distal part, suggesting that the oxidation conditions and/or their Fe contents in hydrothermal fluids varied during K-alteration.

Chemical compositions of associated K-feldspar, illite, actinolite, and titanite are given in Table 4. As mentioned before, K-feldspar and illite are products of K-alteration pertained to the formation of pinkish epidote and brownish chlorite, and actinolite is a product of early propylitization. K-feldspar in veins showed an adularia-like form (Fig. 4b) and was almost pure KAlSi$_3$O$_8$ (more than Or$_{84}$). Illite contained somewhat Fe and Mg, which may be due to the relict of original chlorite. Actinolite was rich in Mg. Titanite contained insignificant amounts of Mn. Chemical compositions of calcite, dolomite, and siderite as well as hematite and pyrite were not determined in the present study.

**Formation conditions**

The formation temperature of chlorite coexisting with quartz can be estimated by currently developed thermodynamic (Vidal et al., 2001, 2006; Lanari et al., 2014) and semi-empirical (Inoue et al., 2009; Bourdelle et al., 2013; Lanari et al., 2014) chlorite geothermometers. The two geothermometers are based on different assumptions in terms of selected endmembers and site ordering models of cations. Whatever the methods, however, the estimated temperatures for chlorites formed at low temperatures (<400 °C) result in values similar to each other (e.g., Bourdelle et al., 2013; Lanari et al., 2014; Vidal et al., 2016). Thus, as a first approximation, the temperatures of chlorite formation were estimated using semi-empirical methods on the basis of assumption of chlorite-quartz-fluid equilibrium. In the semi-empirical methods, Inoue’s geothermometer (Inoue et al., 2009) requires the independent determination of ferric iron contents in chlorite, whereas Bourdelle’s (Bourdelle et al., 2013) does not need the information of ferric iron contents. The average temperatures of chlorite formation estimated by Bourdelle’s geothermometer ranged from 256 to 378 °C for greenish chlorites and from 227 to 301 °C for brownish chlorites (Table 3). The above estimated value of 378 °C for the sample at 837.4 m exceeds the upper limit temperature (<350 °C) to which the semi-empirical method is applicable (Bourdelle and Cathelineau, 2015). While, a similar value was given using Lanari’s geothermometer (Lanari et al., 2014). By the way, NEDO (1991) documented homogenization temperatures of fluid inclusions in vein quartz or calcite in adjacent propylite rocks; the average values were 315 °C (range 243–350 °C) for quartz in the sample at 767.6 m, 231 °C (range 204–257 °C) for calcite in the sample at 783.5 m, 235 °C (range 208–257 °C) for calcite in the sample at 846.6 m, and 289 °C (range 266–315 °C) for quartz in the sample at 964.6 m. Although comparison between the two types of temperature data is strictly impossible because of different sampling depths, minerals used, and paragenetic ambiguity, the two data are similar to each other within the errors. It is suggestive that the formation temperature of brownish chlorite formed during...
### Table 2. Chemical compositions of epidotes

| Depth   | 792.7 m | 837.4 m | 880.5 m | 888.2 m | 996.5 m | Pinkish | 837.4 m | 897.7 m |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Color   | Greenish | Greenish | Greenish | Greenish | Greenish | Greenish | Greenish | Greenish |
| N       | 15      | STD     | core    | rim     | 6       | STD     | 15      | STD     |
| SiO₂    | 36.97   | 0.42    | 36.71   | 37.30   | 36.62   | 0.35    | 38.14   | 0.26    |
| Al₂O₃   | 22.34   | 1.90    | 21.98   | 25.10   | 22.49   | 1.15    | 24.14   | 0.76    |
| TiO₂    | 0.17    | 0.21    | 0.15    | 0.16    | 0.10    | 0.08    | 0.12    | 0.09    |
| Fe₂O₃   | 13.87   | 2.67    | 14.20   | 9.71    | 14.37   | 1.87    | 15.01   | 1.81    |
| MgO     | 0.16    | 0.14    | 0.48    | 0.21    | 0.18    | 0.18    | 0.20    | 0.11    |
| Mn₂O₃   | 0.25    | 0.13    | 0.38    | 0.46    | 0.29    | 0.12    | 0.30    | 0.17    |
| CaO     | 23.02   | 0.34    | 22.54   | 23.08   | 23.19   | 0.32    | 23.36   | 0.40    |
| K₂O     | 0.05    | 0.04    | 0.10    | 0.06    | 0.05    | 0.06    | 0.03    | 0.04    |
| Na₂O    | 0.01    | 0.02    | 0.00    | 0.00    | 0.03    | 0.03    | 0.03    | 0.04    |
| Total   | 96.84   | 0.78    | 96.54   | 96.08   | 98.33   | 0.26    | 99.08   | 0.55    |

| O = 12.5 |
|----------|

| Element | 792.7 m | 837.4 m | 880.5 m | 888.2 m | 996.5 m | Pinkish | 837.4 m | 897.7 m |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Si      | 2.99    | 0.01    | 2.98    | 2.99    | 3.00    | 0.01    | 3.00    | 0.01    |
| Al      | 0.01    | 0.02    | 0.01    | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Fe      | 0.03    | 0.00    | 0.06    | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Ti      | 0.01    | 0.01    | 0.02    | 0.02    | 0.02    | 0.02    | 0.02    | 0.02    |
| Mg      | 0.00    | 0.00    | 0.01    | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Ca      | 0.00    | 0.02    | 0.01    | 0.01    | 0.01    | 0.01    | 0.01    | 0.01    |
| K       | 0.00    | 0.00    | 0.01    | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| Σ       | 3.01    | 0.04    | 3.01    | 3.02    | 3.02    | 3.02    | 3.02    | 3.02    |

| Σ charge| 25.01   | 24.99   | 24.99   | 25.00   | 24.99   | 25.00   | 25.00   | 25.00   |

| Al fraction | 0.712 | 0.055 | 0.702 | 0.794 | 0.706 | 0.037 | 0.743 | 0.018 |
| Fe fraction | 0.283 | 0.056 | 0.290 | 0.196 | 0.288 | 0.037 | 0.251 | 0.017 |
| Mn fraction | 0.005 | 0.003 | 0.008 | 0.009 | 0.006 | 0.003 | 0.007 | 0.004 |
Table 3. Chemical compositions of chlorites

| Depth       | 792.7 m | 808.9 m | 837.4 m | 880.5 m | 837.4 m | 897.7 m |
|-------------|---------|---------|---------|---------|---------|---------|
| N           | 19 STD  | 21 STD  | 4 STD   | 14 STD  | 16 STD  | 12 STD  |
| SiO₂        | 28.57   | 27.43   | 24.97   | 27.82   | 28.70   | 30.27   |
| Al₂O₃       | 18.01   | 17.96   | 20.42   | 18.19   | 18.65   | 18.12   |
| TiO₂        | 0.05    | 0.07    | 0.05    | 0.04    | 0.06    | 0.05    |
| FeO*        | 19.45   | 26.90   | 24.48   | 23.41   | 15.17   | 8.59    |
| MgO         | 19.08   | 13.97   | 13.89   | 15.74   | 20.76   | 27.36   |
| MnO         | 0.59    | 0.65    | 0.48    | 0.67    | 0.63    | 0.49    |
| CaO         | 0.13    | 0.16    | 0.09    | 0.23    | 0.22    | 0.11    |
| K₂O         | 0.02    | 0.07    | 0.01    | 0.05    | 0.04    | 0.02    |
| Na₂O        | 0.10    | 0.14    | 0.00    | 0.04    | 0.03    | 0.04    |
| Total       | 85.99   | 87.35   | 84.38   | 86.19   | 84.25   | 85.03   |

O = 14

| Component | Percentage |
|-----------|------------|
| Si        | 2.97       |
| Al(IV)    | 1.03       |
| S         | 4.00       |
| Al(VI)    | 1.18       |
| Mg        | 2.96       |
| Mn        | 0.05       |
| Fe        | 1.69       |
| Ti        | 0.00       |
| ΣOct      | 5.89       |
| Ca        | 0.01       |
| Na        | 0.02       |
| K         | 0.00       |
| Mg ratio* | 0.63       |
| Temp (°C)* | 273       |
| Fe²⁺/ΣFe** | 0.13      |

* Total Fe as FeO. ** Mg/(Mg + Fe + Mn) ratios. † Temperature of chlorite formation estimated by Bourdelle’s geothermometer (Bourdelle et al., 2013). ## Estimated Fe³⁺/ΣFe (see text).
– alteration stage was almost similar to those of greenish chlorites formed by early propylitization, possibly at 230–300 °C under pressure conditions along the vapor–liquid equilibrium curve for water ($P_{\text{sat}}$). It is noticeable that the formation temperature of brownish chlorites at 837.4 m depth is lower than those at 897.9 m depth. Since the thermodynamic and semi-empirical geothermometers provide similar estimates of formation temperatures, we can assume that the formation temperatures estimated by Bourdelle’s geothermometer are the same as those by Inoue’s. Then the Fe$^{3+}$/ΣFe ratios can be in turn estimated to be 0.05–0.13 for greenish chlorites and 0.25–0.26 for brownish chlorites (Table 3). The result that brownish chlorites formed by K–alteration contain not only less total Fe but also more Fe$^{3+}$ compared to greenish chlorites reveals that the formation of brownish chlorites occurred under more oxidative conditions than those for propylitization.

Physicochemical conditions of the alteration related to the formation of pinkish epidotes and brownish chlorites, except for the formation temperature described above, are not always correctly estimated only from the observed mineral assemblages because of dissipation of the participated fluids. NEDO (1991) documented compositions of fluid recovered from NB–3, but this fluid may not be the same as those participated to the formation of pinkish epidotes and brownish chlorites in NB–1 because pinkish epidotes were not recognized in the K–alteration zone of NB–3 (Fig. 3) but also lower temperatures (<190 °C) of the recovered fluids than the estimated formation temperatures for chlorite and homogenization temperatures of fluid inclusions in NB–1. Nevertheless, judging from the mineral assemblages of epidote, chlorite, K–feld-

Table 4. Chemical compositions of K–feldspar, illite, actinolite, and titanite

| Mineral | K–feldspar | Illite | Actinolite | Titanite |
|---------|------------|--------|------------|----------|
| Depth   | 837.4 m    | 808.9 m | 996.5 m    | 808.9 m  |
| N       | 6          | 8       | 5          | 1        |
| SiO$_2$ | 64.57      | 0.31    | 47.98      | 2.00     | 55.29 | 1.29 | 31.67 |
| Al$_2$O$_3$ | 18.58 | 0.20    | 29.42      | 1.15     | 1.47  | 0.21 | 6.57  |
| TiO$_2$ | 0.08       | 0.06    | 0.23       | 0.15     | 0.10  | 0.08 | 31.82 |
| FeO     | –          | –       | –          | 8.46     | 2.23  | 1.22 |
| Fe$_2$O$_3$ | 0.11  | 0.11    | 4.03       | 0.69     | –     | 0.00 |
| MgO     | 0.08       | 0.12    | 2.03       | 0.28     | 17.14 | 1.60 | 0.00  |
| MnO     | 0.01       | 0.02    | 0.03       | 0.02     | 0.71  | 0.42 | 0.00  |
| CaO     | 0.00       | 0.00    | 0.19       | 0.12     | 13.02 | 0.64 | 28.47 |
| K$_2$O  | 15.92      | 0.04    | 9.43       | 0.38     | 0.05  | 0.06 | 0.06  |
| Na$_2$O | 0.43       | 0.06    | 0.06       | 0.10     | 0.00  | 0.00 | 0.00  |
| Total   | 99.78      | 0.51    | 93.39      | 3.38     | 96.25 | 1.94 | 99.81 |

$O = 8$ $O = 22$ $O = 23$ $O = 5$

$\Sigma$ Si 2.99 0.01 6.51 0.06 7.92 0.02 1.03
Al(IV) 1.01 0.01 1.49 0.06 0.08 – –
$\Sigma$ 4.00 8.00 8.00 1.03
Al(VI) 0.00 – 3.21 0.08 0.17 0.03 0.25
Mg 0.01 0.01 0.41 0.05 3.66 0.27 0.00
Mn 0.00 0.00 0.00 0.00 0.09 0.05 0.00
$Fe^{3+}$ – – – 1.02 0.29 0.03
$Fe^{2+}$ 0.00 0.00 0.41 0.08 – –
Ti 0.00 0.00 0.02 0.01 0.01 0.01 0.78
$\Sigma$ – 4.05 4.95 1.06
Ca 0.00 0.00 0.03 0.02 2.00 0.08 0.99
Na 0.04 0.01 0.01 0.02 0.00 0.00 0.00
K 0.94 0.00 1.63 0.07 0.01 0.01 0.00
$\Sigma$ 0.98 1.67 2.01 0.99

* Total Al.
saturated pressure ($P_{sat}$), and quartz present. Thermodynamic data used in the calculations were cited from Barton (1984), Hayba et al. (1985), and Plumlee (1994). Shaded square is the estimated redox and pH conditions of fluids responsible for the formation of pinkish epidotes associated with brownish chlorites, K-feldspar, illite, and probably calcite. Color version is available online from http://doi.org/10.2465/jmps.161229.

Figure 8. Log $a_{H_2O}(aq)$ versus pH diagram at 250 °C, liquid-vapor saturated pressure ($P_{sat}$), and quartz present. Thermodynamic data used in the calculations were cited from Barton (1984), Hayba et al. (1985), and Plumlee (1994). Shaded square is the estimated redox and pH conditions of fluids responsible for the formation of pinkish epidotes associated with brownish chlorites, K-feldspar, illite, and probably calcite. Color version is available online from http://doi.org/10.2465/jmps.161229.

In addition, the pH values de...

Finally, based on the mineral assemblages and mineral compositions described above, we tentatively propose the redox and pH conditions of fluids pertaining to the K-alteration formed pinkish epidotes and brownish chlorites as shown in Figure 8. The conditions are roughly as follows: at 250 °C and $P_{sat}$, 6.5 < pH < 7.5 and $-6.5 < \log a_{H_2O}(aq) < -5.5$. The latter corresponds to $-32.5 < \log a_{H_2O}(aq) < -30.5$. The physicochemical conditions are as a whole similar to those estimated for many adularia-sericite type epithermal ore deposits (e.g., Heald et al., 1987), though the Fe, S, and Cl contents in fluids may be lower than those in epithermal ore-forming fluids.

CONCLUDING REMARKS

Pinkish epidotes were found in a geothermal well NB-1, Noboribetsu, Hokkaido. The epidotes have low Mn$^{3+}$ contents ranging from 0.00 to 0.08 atoms per formula unit, and the color changed from pale yellow to pink with increasing Mn under low Fe$^{3+}$ contents, for instance, within the ranges less than 28 mol% of Ca$_3$Fe$_2^+$Si$_2$O$_7$(OH) component.

In the Noboribetsu area of a geothermal field, the pinkish epidote occurs with brownish Fe-poor chlorite, K-feldspar, illite, and quartz; the chlorite additionally has greater Fe$^{3+}$ in structure relative to those in the prevailing propylite. The present study suggests that the formation of the Noboribetsu pinkish epidotes took place in epithermal systems which were under oxidative conditions in addition to low Fe contents in hydrothermal fluids. A more detailed study involving determination of quantitative Fe$^{3+}$ distribution in fine-grained chlorite will be required to consider the dynamics of fluid-rock interaction in the Noboribetsu hydrothermal system.

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SUPPLEMENTARY MATERIALS

Color version of Figures 1–8 is available online from http://doi.org/10.2465/jmps.161229.

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