

## HYDROTHERMAL ALTERATION AND SCHEELITE MINERALISATION ASSOCIATED WITH THE BARRYTOWN PLUTON, NORTH WESTLAND, NEW ZEALAND

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### Abstract

The 'S' type Barrytown biotite granite pluton which intrudes Lower Ordovician greywacke and shales is exposed near its original roof level. The pluton is internally zoned from a biotite-rich margin to an acid core. Mild pervasive hydrothermal alteration which affects much of the pluton comprises 3 distinct varieties, early propylitic alteration (chlorite-sericite  $\pm$  clinozoisite, sphene) was concentrated above the NW-SE trending, residually warm pluton core, while later intermediate argillic alteration (kaolinite, illite-tourmaline) developed in the vicinity of roof contacts due to trapping and condensation of acid volatiles. Quartz-tourmaline veins and associated greisen selvages (quartz-muscovite-rutile in granite, quartz-muscovite-tourmaline in metasediments) are restricted to, and apparently postdate, the central clinozoisite-sphene part of the propylitic zone, and contain minor scheelite and rare wolframite, cassiterite, molybdenite and chalcopyrite. Abundant secondary Ti-phases may have held magmatic Sn, W in situ during alteration of biotite, preventing effective leaching and potential ore concentration.

### INTRODUCTION

Granitoid plutonism in New Zealand occurred primarily in the mid-Paleozoic and early Cretaceous. Those granitoids of Paleozoic age appear to be dominantly of 'S' type (Karamea Suite) and are associated with minor W-Sn mineralisation. Those of Cretaceous age comprise both I (Separation Point Batholith) and intermediate I/S (Rahu Suite) varieties, outliers of the former containing weak Mo  $\pm$  Cu mineralisation (Tulloch, 1983). A number of W-Sn prospects associated with granites in New Zealand have been investigated in recent years, but no such mineralisation has ever resulted in significant mining (Brathwaite & Pirajno 1985, Williams 1974). Scheelite generally predominates over wolframite and cassiterite (see also Hutton 1950) and together with a general lack of fluorite and topaz, suggests regionally low activity of fluorine (Burt, 1981).

The 4 km<sup>2</sup> Barrytown biotite granite pluton (Tulloch, in prep.) subconcordantly intrudes a greywacke and shale sequence of the Lower Ordovician Greenland Group (lower grade greenschist facies) (Laird 1972). The pluton is now exposed near its original roof level—a small area of horizontal roof is preserved, with sidewall contacts dipping 45–60° outwards. Contoured plots of modal mineral proportions define an internal zoning from a biotite-, plagioclase-rich rim to a microcline-rich core zone, the NW-SE axis of which also subparallels the strike of the country rocks (Fig. 1). Geochemical models of this zonation (6.9–18.6% modal biotite, 67.83–71.81% SiO<sub>2</sub>) are consistent with an origin by in situ fractionation by marginal accumulation, or batch partial melting combined with restite unmixing. Petrographic and chemical features also indicate the pluton is 'S' type and belongs to the mid-Paleozoic Karamea Suite (Table 1). Apart from obviously enriched areas the pluton averages 10 ppm Sn (4 analyses) and 9 ppm

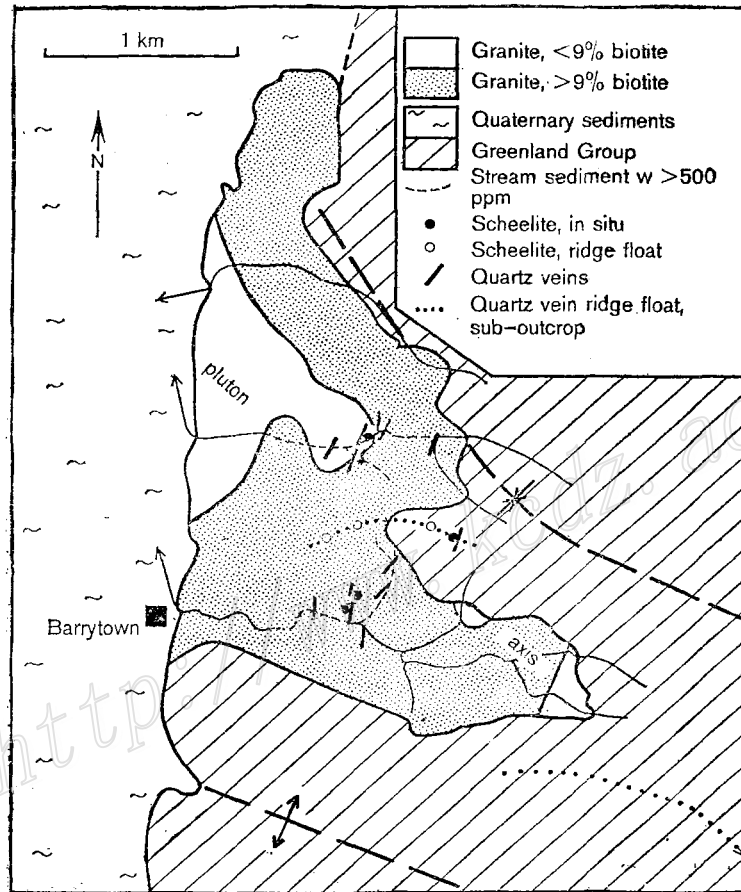


Fig. 1. Geological map of Barrytown biotite granite pluton. For regional location see Tulloch 1983, Fig. 3. Stream sediment W data from unpublished map of Carpentaria Exploration (Australia) Ltd. Greenland Group fold axes modified after Laird (1972). Pluton axis defined by modal zoning and pluton form (Tulloch, in prep.).

TABLE 1. Representative analyses of Barrytown Granite, greisenised granite and greisenised Greenland Group roof rocks

	By11 Granite*	1006 Endogreisen (granite)	1009 Exogreisen (greywacke)	1014 Exogreisen (argillite)
SiO <sub>2</sub>	70.28	73.34	63.62	58.70
TiO <sub>2</sub>	0.50	0.33	0.32	0.63
Al <sub>2</sub> O <sub>3</sub>	14.31	14.29	16.53	22.13
Fe <sub>2</sub> O <sub>3</sub>	0.55	0.58	0.99	3.69
FeO	2.72	0.85	5.00	2.22
MnO	0.08	0.01	0.04	0.02
MgO	0.92	0.47	3.23	3.47
CaO	1.40	0.20	0.55	0.27
Na <sub>2</sub> O	2.92	2.22	1.55	0.95
K <sub>2</sub> O	4.89	5.12	3.51	3.73
P <sub>2</sub> O <sub>5</sub>	0.17	0.10	0.14	0.08
LOI	1.00	1.75	3.48	3.62
<b>Total</b>	<b>100.04</b>	<b>99.26</b>	<b>99.41</b>	<b>99.51</b>
Y	—	22	74	12
Rb	280	322	163	238
Pb	—	43	30	18
Ga	—	20	22	34
Th	—	29	15	14
U	—	11	4	2
Cr	27	9	93	97
V	—	19	104	130
Ba	334	262	492	442
Zn	60	39	117	78
Cu	—	32	39	37
Ni	—	5	36	20
Nb	—	17	16	9
Zr	198	145	166	99
Sr	95	50	94	370
La	100	50	100	50
Yb	5	2	5	2
B	40	150	4,200	15,000
W	9	—	18	—
Sn	8	10	—	8
Li	91	95	86	—
Be	6	10	4	—
As	37	49	24	—

\* Note that By11 is representative of an intermediate core-rim composition and is not directly equivalent to the precursor of 1006.

La, Yb, B, Sn Sn by semiquant emission spectrography, Li, Be and As by AA. Others by XRF.

W (2 analyses) compared with 3 ppm Sn and 1.5 ppm W for world averages in low-Ca granites (Jackson, 1979).

### QUARTZ VEINS AND MINERALISATION

A zone defined by abundant quartz veins and including all scheelite occurrences (Fig. 1) is coincident with the NW-SE pluton core elongation. Most veins are either vertical or slightly west dipping and trend  $10^{\circ}$ – $60^{\circ}$ . The most significant joint direction in the granite also strikes approximately  $35^{\circ}$  with variable dips to NW. Thus the dominant fracturing within the pluton was at a high angle to the long axis of the pluton and its internal zoning. Situated within and above the core zone this fracturing was probably consequent upon retrograde boiling of volatiles concentrated in the core, with rupture occurring vertically and constrained parallel to the direction of maximum horizontal principle stress. Such fracturing limits the depth of emplacement to less than approximately 7 km (Burnham and Ohmoto 1980). As the veins are perpendicular to the axes of folds in the enclosing Greenland Group trend it is concluded that the country rock structure controlled not only the gross and detailed pluton form, but that it also confined the minimum horizontal stress to a NW-SE direction. Quartz veins range up to approximately 50 cm thick but most are less than 10 cm, with a tendency to form sheeted swarms of 1–3 metres total width containing up to 15 veins per metre of individual thickness 0.5–2 cm. Mineralisation occurs within quartz-tourmaline (dravite) veins or their associated greisenised wall rocks.

No other F-bearing phases other than tourmaline were observed save the association of topaz with the single occurrence of wolframite. Scheelite, pyrite and tourmaline occur in both quartz veins and associated greisen. In the latter situation the occurrence of scheelite replacing plagioclase indicates a local Ca source, and suggests that the extent of scheelite formation was at least in part controlled by this rather limited source. The only cassiterite observed in situ occurs in greisen. All other Fe, Ti oxides and sulphides are restricted to greisen.

Wolframite occurs as black bladed crystals up to 2 cm long in a single quartz-tourmaline-muscovite-topaz-pyrite vein where it is partly replaced and/or followed by scheelite and pale yellow tungstite. Wolframite compositions (microprobe) range from  $\text{Fe}_{.65}\text{Mn}_{.31}\text{Mg}_{.03}$  (core) to  $\text{Fe}_{.60}\text{Mn}_{.37}\text{Mg}_{.03}$  ( $\text{WO}_4$ ) (rim).

Other ore minerals occurring in greisen include, in approximate decreasing order of abundance: pyrite, marcasite, rutile, hematite, pyrrhotite, arsenopyrite + minor pharmacosiderite, chalcopyrite (+covellite-bornite), molybdenite and

magnetite.

Gold-quartz veins at Croesus Knob, 6 km to the SE and 1 km higher may represent an outer zone of the Barrytown system.

### HYDROTHERMAL ALTERATION

Much of the pluton is mildly pervasively altered, although there is great variation even on a thin section scale.

The distribution of three distinct alteration zones—propylitic, greisen, and intermediate argillic—are summarised in Figure 2. Map showing the distribution of individual alteration phases are contained in an NZGS report in preparation. Hydrothermal alteration clearly overprints contact metamorphic biotite, andalusite and hornfelsic texture, and the intermediate argillic zone appears to postdate the propylitic zone, at least in part. The assemblage rutile+calcite included within greisen muscovite suggests that the parent biotite had already been replaced by

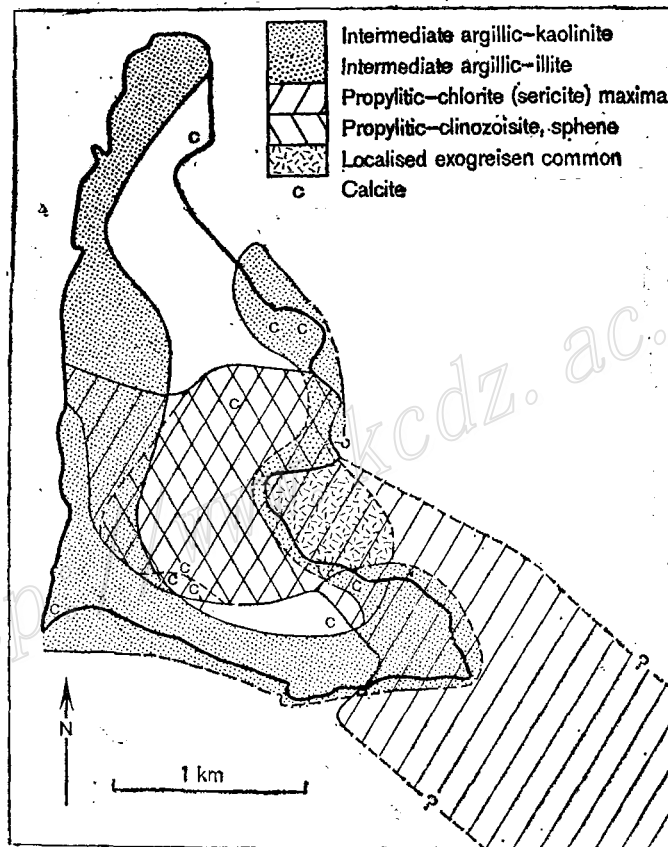
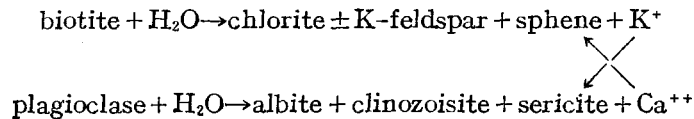


Fig. 2. Hydrothermal alteration zones in the Barrytown pluton and surrounding Greenland Group metasedimentary rocks. c = calcite. Localised endogreisen contained within clinozoisite-sphene part of propylitic zone.

chlorite and sphene and thus greisen alteration also postdates propylitic alteration.

The propylitic zone parallels the postulated zoning and elongation of the pluton at depth. Greisen alteration is strongly localised around quartz veins which are restricted to the higher grade part of the propylitic zone. Sporadic minor calcite occurs in all zones.

Propylitic alteration is defined as a zone in which greater than two thirds of the biotite in thin section has been chloritised. A central subzone also contains clinozoisite and sphene. Although poorly constrained outside the pluton by sample distribution, the propylitic zone extends to the SE, coincident with the postulated SE elongation of the subsurface pluton. There is a strong regional coincidence of chlorite after biotite, and sericite after plagioclase maxima within the pluton, which together with the same spatial connections observed on a thin section scale indicates the coupled reaction;



which in turn suggests that such alteration was largely isochemical, with respect to major elements. Clinozoisite occurs in altered plagioclase ( $\text{Ps}_{0-14}$ ) and rarely in chloritised biotite ( $\text{Ps}_{10-15}$ ). Chlorite distinctly pseudomorphs biotite and has a similar Fe/Mg ratio of 63—64. Ti released from biotite is retained in chlorite as a separate Ti-phase which is sphene or sphene/anatase in the propylitic zone. Outside the propylitic zone core, in the kaolinite and weaker chloritic alteration the Ti-phase is anatase, aggregates of which occasionally appear to represent pseudomorphs after sphene lozenges.

The sphene is notable for its high Al-content;  $\text{Al}_2\text{O}_3$  reaching 8.3% (cf. Tulloch 1979). Contents of Sn and W reach 0.28 and 0.25 oxide % in sphene, and 0.73 and 1.02 respectively in anatase. Work is currently underway to clarify whether this Sn and W can be accounted for by the parent biotite composition, or whether Sn and W have been added or removed from the biotite-chlorite pair. If Sn and W were derived from the host biotite, then the extent of their removal in solution from the biotite site (and potential concentration as an ore deposit) may have been partly controlled by the amount of Ti available to form secondary Ti-phases, into which the Sn, W is captured in situ. Thus relatively high  $\text{TiO}_2$  at Barrytown (0.38%  $\text{TiO}_2$  at 71.81%  $\text{SiO}_2$ ) may have augmented against effective leaching compared with, for example, the Yanshanian granites of SE China (0.22%  $\text{TiO}_2$  at 72.65%  $\text{SiO}_2$ , Yan et al, 1980) and the Cornubian Batholith of Cornwall (e. g. 0.24%  $\text{TiO}_2$  at 71.45%  $\text{TiO}_2$ , Alderton et

al, 1980).

**Endogreisen** alteration is restricted to the margins of quartz veins, forming localised zones less than 1—2 m thick. They occur within, but probably affect less than approximately 5% of, the propylitic-clinozoisite subzone. Muscovite + rutile completely replaces biotite and chlorite. Microprobe analyses of rutile reveal up to 0.3% SnO<sub>2</sub> and 0.62 WO<sub>3</sub>. Muscovite also completely replaces plagioclase and partly replaces microcline, the assemblage trending towards quartz-muscovite ± tourmaline and the oxide-sulphide phases discussed above.

**Exogreisen** alteration in the Greenland Group roof rocks is dominated by the assemblage quartz-tourmaline-sericite with accessory anatase/rutile (?) and hematite/goethite. Altered argillites are preferentially metasomatised by boron-rich fluids, and tourmaline (intermediate schorl-dravite) may account for 60—70% of such rocks. While Fe and Mg from altered biotite are largely removed from the endogreisen they are held in tourmaline in the exogreisen whose crystallisation is favoured by the higher Al-content of the sedimentary rocks, and greater Al-metasomatism.

Chemical analyses of endo- and exogreisen document significant metasomatism (Table 1, Tulloch, unpublished data). The endogreisen is enriched relative to the original rim facies granite in SiO<sub>2</sub>, Fe<sup>3+/2+</sup>, K, Rb, Pb, U, B, and is depleted in TiO<sub>2</sub>, Fe, MnO, MgO, CaO, P<sub>2</sub>O<sub>5</sub>, Y, Cr, V, Ba, Zn, Sr and La (mass-balance calculations by the method of Gresens 1967). Note that Ti, Zr, P, La and Y appear to be far from immobile in this situation. Greisenised roof rocks exhibit an increase in Al<sub>2</sub>O<sub>3</sub>, Fe<sup>3+/2+</sup>, Rb, Sr, Sn, Li, Be, B and As; Y, Pb and Ba are depleted (cf. Nathan 1976).

The **intermediate argillic** zone is largely defined by the occurrence of highly disordered kaolinite partly replacing plagioclase. The zone appears to be strongly controlled by the pluton/country rock interface and extends further into the pluton than the host. In the country rock biotite is often relatively unaltered, and minor tourmaline is generally present. A subordinate illite-tourmaline sub-zone occurs within the pluton close to the roof, as defined by the presence of illite rather than kaolinite, replacing plagioclase. Illite also replaces biotite, or chlorite after biotite, in rocks where calcite is abundant.

### NATURE OF THE HYDROTHERMAL FLUID

The relative positions of the three alteration zones are plotted on an activity ratio phase diagram in Fig. 3. Intermediate argillic kaolinite-bearing assemblages have resulted from relatively acid, low pH fluids at temperatures less than 300 °C, although the illite subzone suggests higher temperatures prevailed

in this central region. The position of the K-mica field indicates moderately acid conditions prevailed during greisen alteration, probably at temperatures above 300 °C. The formation of wolframite requires a pH in the range 3.6–6.2 (at 300 °C, Horner 1979), although the general occurrence of scheelite rather than wolframite indicates that  $a_F$  was not especially high (Burt, 1981). High and progressively higher states of oxidation upwards in the system are evidenced by whole rock  $Fe^{2+}/Fe^{3+}$  ratios of 0.6 and 0.3 in the upper pluton and Greenland Group roof respectively, compared to unaltered values of approximately 0.8 in both pluton and host. Co-existence of pyrite with minor pyrrhotite, hematite and magnetite indicates later evolution of a more neutral to possibly alkaline fluid (Henley et al. 1984), probably due to separation of acid volatiles by boiling. Experimental determination of sphene-rutile- $CO_2$  equilibria (Hunt & Kerrick 1977) indicates the formation of rutile could be due to either high  $CO_2$  or relatively lower temperatures compared to the sphene-bearing propylitic zone (the latter may result from 'cold' meteoric water flowing through major fractures in, and cooling, a 'hot' pluton).

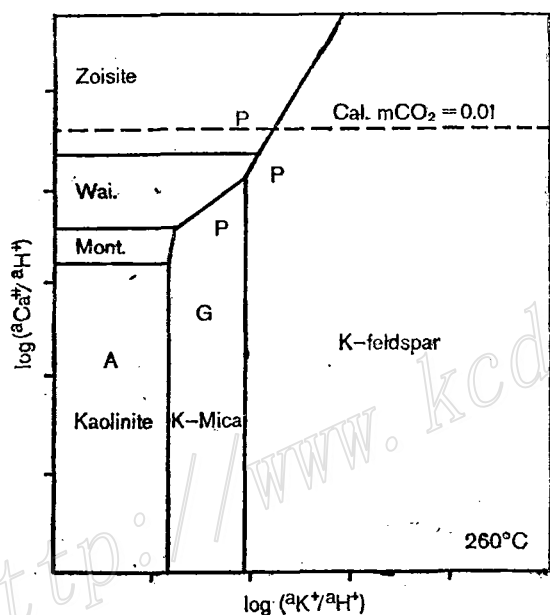


Fig. 3. Activity diagram showing postulated fluid compositions for intermediate argillic (A), greisen (G), and propylitic (P) alteration assemblages at Barrytown. Cal = calcite precipitation line at  $m_{CO_2} = 0.01$  (Ellis and Mahon, 1977).

The propylitic zone assemblage (Fig. 3) indicates a more neutral fluid, with low  $CO_2$  ( $m_{CO_2} < 0.03$ ). Low oxygen fugacity (low Ps content of epidote and



unaltered bulk rock  $Fe^{2+/3+}$ ) shows that the fluid composition was buffered by the rock composition. The apparent lack of significant cation metasomatism is consistent with a redistribution of components on a mm-scale. Development of clinozoisite suggests that the temperature of this part of the propylitic alteration exceeded 250°C (Browne 1978).

### FLUID SOURCE AND PATHLINES

The observed hydrothermal alteration could result either from (1) 'cold' (meteoric?) fluid passing through a residually hot pluton core, (2) from 'in situ' retrograde alteration or re-equilibration of a cooling pluton reacting with its own exsolved fluid, or (3) from the passage of 'hot' (magmatic?) fluids which raised the rock temperature. The coincidence of the hydrothermal alteration zones with the pluton's magmatic core, and the low thermal conductivity and permeability of the large intervein regions suggest that (3) is unlikely. The geometry of the intermediate argillic alteration zone indicates that the hydrological situation and temperature gradient in the concave upper part of the pluton promoted the trapping and condensation of volatiles rich in acid gases, to produce a low pH fluid.

It is assumed that both magmatic and meteoric fluids were to some extent involved in the Barrytown system (e.g. Henley and McNabb 1978 and references therein). Meteoric fluids could potentially provide a source of B by leaching from the Greenland Group host sediments (cf. Ellis & Mahon 1966), which contain 20—80 ppm B (Tulloch, unpublished data on 4 unaltered samples).

Model (1) above might have been realised by drawing neutral meteoric fluid into the cooling pluton producing propylitic alteration as the fluid warmed (Giggenbach 1984, Taylor and Fryer 1980, Ford and Green 1977). Some of this reaches major fractures and mixes with a more acid magmatic fluid to deposit quartz-scheelite veins and to produce greisen alteration as it rises via a hydrothermal convection cell (eg. Cathles 1977). Acid alteration in the roof may result from gas separation from a purely magmatic fluid, or from a combined magmatic-meteoric fluid.

Model (2) is supported by the relative homogeneity and impervious nature of much of the pluton, which suggests that 'in situ' late magmatic aqueous fluid may be responsible for the pervasive propylitic zone alteration. Although 'regionally' pervasive, propylitic alteration within individual thin sections is irregular with virtually all rocks containing some unaltered biotite, arguing strongly against significant bulk transfer of fluid through the intervein regions.

Oxygen isotope studies are planned to test the above models.

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# 与新西兰北韦斯特兰巴里汤侵入岩体 有关的热液蚀变和白钨矿化

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## 摘 要

侵入奥陶纪下部硬砂岩和页岩的‘S’型巴里汤黑云母花岗岩体在接近其原始顶板位置出露地表。该岩体从富黑云母的边缘至酸性的核部呈内部分带现象。影响很大一部分岩体的弱弥漫型热液蚀变由三种有明显区别的类型组成：早期绿磐岩化（绿泥石-绢云母±斜黧帘石、絹石）集中于北西-南东走向的、当时尚有余温的岩体核部上方，而其后的中性泥质蚀变（高岭石、伊利石-电气石）发育于顶板接触带附近，这是由于捕获和凝聚酸性挥发分造成的。石英-电气石脉及与其有关的云英岩边（花岗岩中的石英-白云母-金红石，变质沉积岩中的石英-白云母-电气石）仅见于绿磐岩的中央斜黧帘石-絹石部分，并且明显地晚于后者生成。它们含有少量的白钨矿和很少的黑钨矿、锡石、辉钼矿和黄铜矿。在黑云母蚀变过程中，丰富的钛相矿物可能在原地捕获岩浆的锡和钨，这阻碍了有效的淋滤和矿石的富集。

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