Yimengite of K–Ti metasomatic origin in kimberlitic rocks from Venezuela

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Abstract

This second recorded occurrence of yimengite, $K(Cr, Ti, Fe, Mg, Al)_{12}O_{19}$, is in a Precambrian kimberlitic sill in the Guaniamo District of Bolivar Province, Venezuela. The paragenesis is similar to that of the type area in Shandong Province, China, where the mineral is in kimberlite dykes. At both localities the yimengite is a K, Ti-bearing metasomatic product of chromium-rich spinel. In the Venezuela rocks the spinels are of the type occurring both as diamond inclusions and as a component of diamond-related Cr-rich garnet harzburgite mantle xenoliths. Yimengite contains significant amounts of barium (up to 3.4 wt.% BaO) and is thus transitional to the recently described mineral hawthorneite, Ba(Cr, Ti, Fe, Mg)₁₂O₁₉. Both members are part of a suite of titanate minerals found in kimberlites and their inclusions which has been described by Haggerty and coworkers; they formed as a result of mantle metasomatism generated by K- and Ba-rich fluids. In Venezuela, metasomatism of this type would appear to be deeper than that usually recorded, namely in the basal lithosphere. The metasomatizing fluids are derived from the underlying, more oxygenated asthenosphere. The host kimberlitic rocks are not significantly enriched in K and Ba, but these elements are concentrated in later micaceous dykes which are conjectured to have been generated within similar metasomatized mantle.

KEYWORDS: yimengite, hawthorneite, spinel, kimberlitic rocks, Venezuela.

Introduction

YIMENGITE, K(Cr, Ti, Fe, Mg, Al)₁₂O₁₉, was discovered in kimberlite dykes in Shandong Province, China, in 1980 (Dong Zhenxin *et al.*, 1983). It occurs as macrocrysts coexisting with chromite and in association with olivine, phlogopite, pyrope, ilmenite, chromium diopside, apatite, zircon, moissanite, and perovskite. On account of its occurrence in kimberlite, and on crystal structure consideration, yimengite is regarded as having formed under 'high' pressure (Peng Zhinzhong and Lu Qi, 1985).

The present occurrence is in a heavy-mineral concentrate from a recently discovered Precambrian weathered kimberlitic sill within the alluvial diamond area of Guaniamo, Bolivar Province, Venezuela (Nixon, Condliffe, Davies, Baker and Baxter-Brown, in preparation). These workers have identified the predominant associated heavy minerals as high-Cr spinel and Cr pyrope of widely varying calcium content. Some heavy minerals usually found in kimberlites, e.g. magnesian ilmenite and titanian pyrope megacrysts, are lacking in the area; trace element compositions of the

Mineralogical Magazine, June 1989, Vol. 53, pp. 305–309 © Copyright the Mineralogical Society rocks are somewhat different from typical kimberlite or indeed lamproite, and have still to be evaluated.

Yimengite is an alteration product of chromium spinel macrocrysts. Although the spinels are abundant, both in the gravels and kimberlitic rocks, examination of over 100 grains revealed only two instances of associated yimengite. Compositionally-similar chromium-rich spinels and chromium-rich pyropes are found as inclusions in diamonds (see review by Meyer, 1985) and in diamond-bearing harzburgite xenoliths (Sobolev *et al.*, 1973; Boyd and Gurney, 1982; Nixon *et al.*, 1987). The chromium spinels within the Venezuela kimberlitic rock are, therefore, interpreted as xenocrysts from disaggregated deep-seated garnet harzburgites.

Yimengite

Figure 1 shows yimengite in contact with chromium spinel. The latter has a spongy appearance which seems to be the intermediate stage in alteration to yimengite.



FIG. 1. Backscattered electron microprobe image showing yimengite (top) in contact with spongy chromium spinel; field of view is 0.5 mm; from kimberlitic sill at Prospect 039, Guaniamo region, Bolivar Province, Venezuela.

The chromium spinels occur as black octahedra, with sharp or rounded edges, or as irregular fragments up to 3 mm across. The small amount of yimengite alteration observed makes physical characteristics difficult to ascertain. Dong Zhenxin *et al.*, 1983, state that yimengite is a black hexagonal mineral which is distinguished macroscopically from chromite by the presence of a welldefined (0001) cleavage. The Venezuelan chromium spinels, however, have a good (111) cleavage and the distinction between the two minerals with the naked eye is not obvious.

A significant aspect of the structure of yimengite is the presence of a large cation site in which K and other *LIL* (large ion lithophile) elements could potentially be accommodated within the deep mantle. There is twice as much K in yimengite as in an earlier described K(Ba) titanate, mathiasite, of the crichtonite group (Haggerty *et al.*, 1983; Haggerty, 1987), which also occurs in the Shandong kimberlites (Jianziong *et al.*, 1984).

The presence of barium in the yimengite from China, although not reported in the original description by Doug Zhenxin *et al.* (1983), is indicated by Haggerty (1987)—see Table 1. In our specimens, the amount of BaO is somewhat greater, in the range 1.8-3.4 wt.% (Table 1; compositions by EMPA). These levels show that up to about 20% of the hawthorneite molecule, Ba(Ti₃Cr₄Fe₄Mg)O₁₉, is present (Grey *et al.*, 1987; Haggerty *et al.*, 1989). Hawthorneite, which occurs in a metasomatized veined phlogopite, Krichterite, lindsleyite (Ba crichtonite group) harzburgite xenolith in kimberlite (from Kimberley district, South Africa) has a magnetoplumbitetype structure similar to that of yimengite (Peng Zhizhong and Lu Qi, 1985; Haggerty *et al.*, 1986; Grey *et al.*, 1987) with the large ion occurring within perovskite-type segments intercalated with spinel-type layers.

The Venezuela yimengite contains a small amount of Sr (mean of eleven analyses, 0.3 wt.% SrO) which is grouped with the other large ions in Table 1.

Metasomatic variations within the Cr(Ti) spinels

Titanium is a major component (c. 30 wt.%TiO₂) of yimengite, and is found in the adjacent spongy chromium spinel in unusually large amounts (7 wt.% TiO₂; cf. <1 wt.% in most chromium spinels, Table 1). Compositionally, the spongy spinel corresponds to a mixture of magnesiochromite (MgCr₂O₄), magnetite (Fe₃O₄), and ulvöspinel (Fe₂TiO₄) in the approximate ratio of 4:1:1.

There is a similar metasomatic alteration of spinel in the generation of hawthorneite as is seen in compositional differences between the spinel which is in contact with hawthorneite, and that which is enclosed by phlogopite within the same harzburgite xenolith (Haggerty *et al.*, 1986).

Although metasomatism produces an increase in Ti, and a decrease in Cr in the spinels of both occurrences, the behaviour of Fe^{3+} (computed) and Al in particular is dissimilar as is shown on page 308.

There are several reasons that could account for the differing ionic enrichment/impoverishment trends of the metasomatic spinels (lower line), not least of which is the influence of compositionally different metasomatizing fluids (see below). Additionally, it should be noted that the spinel (upper line) enclosed in phlogopite BD-3096 could itself have been metasomatically reconstituted (since it contains significant amounts of Ti) during the phlogopite, K-richterite veining episode of the host harzburgite. In this case the original *primary* spinel composition can only be conjectured.

The inverse Ti–Cr relationship resulting from metasomatism in the above spinels has also been demonstrated in two types of spinel occurring as discrete grains in a metasomatized sheared dunite xenolith from Kamfersdam kimerlite (Boyd *et al.*, 1983). The only other element to show significant transfer is Al (Table 1, nos. 8 and 9). However, in this case there is no associated metasomatism of the LIMA [lindsleyite(Ba)–mathiasite(K)] or HAWYIM [hawthorneite(Ba)–yimengite(K)] type.

YIMENGITE FROM VENEZUELA

| | Yimengites | | | Hawthorneite | | Chromium spinels (Ti) | | | | |
|--------------------------------------|------------|-------|--------|--------------|-------|---------------------------|--------|-------|-------|--|
| | 1 | Z | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| co0 1 | 0.00 | tr. | tr. | tr. | <0.01 | n.d. | 0.28 | <0.03 | <0.03 | |
| к20 | 3.75 | 4.47 | 4,50 | 4.31 | 0.45 | | | | | |
| BoO LI | 1.61 | 1.85 | 2.31 | 3.39 | 13,61 | | | | | |
| SrO | - | 0,31 | 0,36 | 0.36 | - | | | | | |
| Si0 ₂ | 0.55 | 0,55 | 0.52 | 0.80 | 0.06 | 0.20 | 0.66 | 0.25 | 0.29 | |
| TiO ₂ | 29,15 | 31.05 | 30,57 | 28.85 | 23,27 | 0.22 | 7.04 | 3.31 | 7.30 | |
| A1203 | 1.61 | 3.87 | 3.61 | 3.95 | 0.22 | 7.70 | 2.17 | 0.75 | 10.1 | |
| Cr203 | 37.06 | 39,08 | 39.37 | 39.31 | 31.41 | 63.75 | 44,65 | 52.5 | 38.8 | |
| Fe203 | - | 1,20* | 2.76* | 4.23* | - | 0.72* | 11.68* | 12.6* | 10.5* | |
| Fe0 | 18.36 | 11.21 | 9.88 | 8.38 | 24.80 | 15.99 | 21.15 | 19.4 | 21.4 | |
| MnO | 0.00 | tr. | - | - | 0.24 | 0.26 | 0.80 | 0.31 | 0.27 | |
| Mg0 | 7.89 | 5.88 | 6.19 | 6,36 | 3.50 | 11.35 | 11.14 | 9.85 | 12.4 | |
| v203 | | | | | | 0.12 | - | - | - | |
| NiO | | | | | | 0.21 | - | 0.21 | 0.25 | |
| ZnO | | | | | | 0.16 | - | - | - | |
| Total^ | 99.98 | 99.47 | 100.07 | 99.94 | 98.25 | 100.68 | 99.57 | 99.2 | 101.3 | |
| Number of cations per 19 oxygen ions | | | | | | Cations per 4 oxygen ions | | | | |
| Co | | - | - | - | | - | 0.010 | - | - | |
| к | | 0.871 | 0.875 | 0.842 | | | | | | |
| Ba | | 0.111 | 0.138 | 0.204 | | | | | | |
| Sr | | 0,028 | 0.032 | 0.032 | | | | | | |
| Si | | 0.084 | 0.080 | 0.122 | | 0.007 | 0.022 | 0.007 | 0.009 | |
| Ti | | 3.571 | 3.503 | 3.320 | | 0.005 | 0.181 | 0.087 | 0.177 | |
| Al | | 0.697 | 0.648 | 0.712 | | 0.298 | 0.087 | 0.031 | 0.383 | |
| Cr | | 4.725 | 4.743 | 4.757 | | 1.656 | 1.205 | 1.450 | 0.990 | |
| Fe ^{3+*} | | 0.138 | 0.317 | 0.488 | | 0.018 | 0.300 | 0.331 | 0.255 | |
| Fe ²⁺ | | 1.434 | 1.259 | 1.074 | | 0.439 | 0.604 | 0.566 | 0.576 | |
| Mn | | - | - | - | | 0.007 | 0.023 | 0.009 | 0.007 | |
| Mg | | 1.341 | 1.405 | 1.449 | | 0.556 | 0.567 | 0.513 | 0,597 | |
| v | | | | | | 0.003 | - | - | - | |
| Ni | | | | | | 0.006 | - | 0.006 | 0.007 | |
| Zn | | | | | | 0.004 | - | - | - | |
| Total | | 13.00 | 13.00 | 13.00 | | 3.00 | 3,00 | 3.00 | 3.00 | |

Table 1. Analyses of yimengite, hawtharneite and related chromium spinels associated with Ti mantle metasamatism (wt.%).

* Ferric iron determined stoichiometrically

tr. trace

^a Totals normalized in Fe³⁺ calculations

LIL Large Ion Lithophile element group

Type Yimengite, kimberlite dyke, Shandong, China (Dong Zhenxin et al., 1983) with BaO addition noted by Haggerty (1987).

3 and 4. Yimengites from kimberlitic rock PNN 5750/039 from 039 prospect Guaniamo District, Bolivar Province, Venezuela. Trace amounts of ZrO₂ and Nb₂O₅ are present.

Hawthorneite from metasamatized, phlagopite, K-richterite-veined harzburgite xenolith, BD 30%, from kimberlite, Bultfontein floors, Kimberley, South Africa (Hoggerty, 1987; other oxides include : Na₂, 0.01; Ta₂O₂, 0.18 and La₂O₂, 0.1).
 Typical high-Cr spinel, Cordero Claim, Guaniamo District, Bolivar Province, Venezuela.

Spongy chromium spinel adjacent to yimengite in kimberlitic rock, Prospect 039, Guoniamo District, Bolivar Province, Venezuela.

8 and 9. High-Cr spinel and Ti-Cr spinel; separate grains in metasomatized dunite xenolith, PHN 4743F, Kamfersdam kimberlite, Kimberley, South Africa (Boyd et al., 1983).



Formation of yimengite from spongy spinel

The formation yimengite involves the incorporation of two components; the spongy spinel which it partly replaces, and elements from the metasomatizing fluid. In the case of hawthorneite, Grey *et al.* (1987) have shown that part of the Cr and Mg in the spinel is replaced by Ti and Ba which form segments of hexagonal $BaTiO_3$ in the dominantly spinel structure. An analogous ionic exchange is shown in yimengite; on an equal oxygen basis this mineral is deficient in Cr and Mg compared with the spongy spinel, and has gained Ti and K (and minor Ba and Sr) from the metasomatizing fluid.

There are, however, some differences in ionic exchange patterns compared with hawthorneite, in part arising from charge balance considerations resulting from the presence of monovalent potassium in the yimengite lattice in place of divalent barium. Thus, counterbalancing high-valent Ti, Cr, and Al are present in greater quantity in yimengite than in hawthorneite (Table 1). Total Fe is less than recorded for yimengite from China and is only about half that found in hawthorneite (Table 1). The comparatively high Fe content in the spongy spinel indicates that this element was replaced in addition to Cr and Mg during yimengite formation.

The calculated Fe^{3+}/Fe^{2+} ratios of both the spongy spinel and the associated yimengite are considerably higher than those of the primary, unaltered Cr spinels suggesting the imposition of a more oxidizing environment during metasomatism (discussed below).

Significance of yimengite

It could be argued that yimengite alteration of the Cr spinel was a result of reaction with the transporting magma. The true nature of the kimberlitic host rock has not yet been ascertained due to its weathered nature, but it has lamproitic affinities (Nixon, Baker, Baxter-Brown, Condliffe, and Davies, in preparation). The rock contains approximately 1.5 wt.% TiO₂, 0.5 wt.% K₂O, and 500 ppm Ba—levels that can be matched with many kimberlites and indeed alkali basaltic rocks, and which are considered to be too low to be effective K, Ba, Ti metasomatizing fluids. On the other hand fresh lamproites average 6.9 wt.% K₂O and 5100 ppm BaO (Bergman, 1987) and crystallize minerals that are chemically comparable with yimengite (and hawthorneite) namely, priderite, (K, Ba) (Ti7,, Fe3+)O16, and jeppeite, (K, Ba)₂(Ti, Fe)₆O₁₃ (Haggerty, 1987). Both jeppeite and priderite (Mitchell and Lewis, 1983) also occur in metasomatized mantle xenoliths and it is difficult to escape the conclusion that metasomatic fluids are reactive both within mantle regions where they are accumulated and within magmas which intercept those regions.

In this respect, it is notable that the Venezuelan kimberlitic rocks are intersected by a younger (0.85 b.y.) lamprophyric dyke which is very enriched in potassium and barium: 4.6 wt.% K₂O; 1.0 wt.% BaO.

The Cr-rich spinel xenocrysts associated with yimengite have been identified, together with Cr-rich pyrope, with diamond-bearing harzburgitic xenoliths occurring in the basal continental lithosphere (Boyd and Gurney, 1982; Nixon *et al.*, 1987). Although xenolithic evidence is desirable, this suggests that the metasomatism has a similar deep-seated origin (c. 150 km). If this is the case then the yimengite is a notable high-pressure sink for K, Ba and Sr at a depth greater than has been estimated for hawthorneite (75–100 km; Haggerty *et al.*, 1986).

It is concluded that the formation of yimengite was not primarily a kimberlite phenomenon but a result of deep lithospheric mantle enrichment, symptoms of which were transmitted to any magma arising from that zone.

Detailed discussion of the source of the fluids

that gave rise to yimengite-type metasomatism (Ti, K, Ba, Sr) is beyond the scope of this article, but see general reviews by Harte (1987), Nixon and Davies (1987), Erlank *et al.* (1987) and Haggerty (1987). However, our inference that yimengite was generated at the base of the lithosphere is compatible with the derivation of the interacting Ti, K, Ba, Sr, *LIL* ions from the immediately underlying asthenosphere. Supporting the contention of Haggerty (1986), the contrasting oxidation state of the spinels implies that the asthenosphere was (and presumably still is) more oxidized than the overlying diamond-bearing Cr-spinel, Cr-garnet harzburgite lower lithosphere in this part of Venezuela.

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