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The purpose of this contribution is to provide an overview of the LIL-bearing Ti-Cr-Fe oxides. Also discussed is the chemistry of the precipitatorial environment which differs from that normally conceived to be present in the upper mantle.

LIL stands for large ion lithophile elements. It includes K, Ba, Ca, Sr, Na, REE, Rb, Pb and U. LIL-bearing Ti-Cr-Fe oxides have been discovered in a few Chinese kimberlites (Zhou et al, 1980, 1982, 1984; Dong et al, 1983). They are crichtonite series, yiemengite, Cr-priderite and so on. The LIL elements, K, Ba, Ca, Sr, REE and Na in these minerals are in significant concentrations, from 1 wt % oxide to 8 wt % oxides. Because of structural flexibility, these mineral are also repositories for refractory elements, such as Ti, Cr, Nb, Zr and Al. Few kimberlite bodies which contain so many LIL-bearing Ti-Cr-Fe oxides have been discovered in the other parts of the world. Only one example, the Jagersfontein kimberlite, South Africa which has a very similar Ba-specific assemblage has been described (Haggerty, 1975; Smyth et al, 1978; Jones et al, 1982). The kimberlites with LIL-bearing Ti-Cr-Fe oxides are similar to others in mineral assemblage. The main rock-forming minerals are olivine, phlogopite and the accessory minerals are diamond, pyrope, chromite, ilmenite, Cr-picroilmenite, perovskite, Cr-diopside, apatite, zircon and magnetite.

The following species of crichtonite have been recognised: (1) mathiasite, K member of crichtonite; (2) lindsleyite, Ba member of crichtonite; (3) loveringite, Ca member of crichtonite. Mathiasite is more common than others and it exhibits some degree of solid solution towards loveringite or lindsleyite (Fig. 1). Although compositional variation or zoning within individual crichtonites is not common, there is a little difference compositionally among grains. A few other mineral inclusions with very high ZrO₂ or K₂O (unidentified) in crichtonite have been found. Major elements in order of decreasing abundance are as follows (by oxide weight percent): TiO₂ 53-60 wt %, Cr₂O₃ 16-20 wt %, FeO 7-11 wt %, ZrO₂ 4-5 wt % and MgO about 4 wt %. These are the small cations occupying the M-formula position in AM₂O₃₈. Other elements in this position are Mn, Al, Nb and so on, but their total content is less than 2 wt %. The large radius cation position is occupied by K₂O, CaO, BaO, SrO, Na₂O and REE, their contents varying in each member of crichtonite (Table 1). More than 30 crichtonite xenocrysts have been analysed, but the pure K, Ba, Ca members have not been found. These crichtonites are named according to the dominant A-site cation in this paper. The contents of small radius cations, such as Fe²⁺, Fe³⁺, Al, Cr, Ti, Mg and Zr, of crichtonites in Chinese kimberlites are different from other members of the crichtonite series, especially for Cr₂O₃, Zr₂O and Nb₂O₅ contents. These crichtonites as high pressure reservoirs for refractory and LIL elements in the upper mantle may be important for understanding the dynamics of fluid movements and mantle metasomatism (Haggerty, 1983).

Yiemengite (K, Ba) (Cr, Ti, Fe, Mg)₁₂O₁₉ in chemical formula and crystal structure is similar to magnetoplumbite which occurs in products of secure radioactive waste disposal. So yiemengite and above crichtonites may have a direct application to such secure disposal, because they all have structural flexibility in hosting large and small cations and they are highly refractory. Typical yiemengite contains K₂O 3.38 wt %, BaO 3.03 wt %, Cr₂O₃ 37.18 wt %, TiO₂ 29.57 wt %, FeO 17.77 wt %, MgO 5.69 wt % as the major oxides. Other oxides present are CaO 0.13 wt %, SrO 0.12 wt %, ZrO₂ 0.04 wt %, Al₂O₃ 1.08 wt %, Nb₂O₅ 1.03, V₂O₅ 0.01 wt %. X-ray study shows it must be a hexagonal symmetry, P6₃/mmc. Cell parameters are a = 5.81 Å, c = 22.94 Å. Yiemengite usually is a homogeneous discrete single crystal. Sometimes a rim of decomposition products around yiemengite is found. Yiemengite was metasomatised and replaced by combinations of subhedral chromite and Cr-priderite (Fig. 2). These chromites contain relatively high titanium (TiO₂ about 6 wt %) and low alumina (Al₂O₃ 2 wt %). They are enriched in magnesium-ulvospinel with minor magnesioferrite. This is indicative of somewhat lower f_{O₂} conditions (Haggerty 1983).

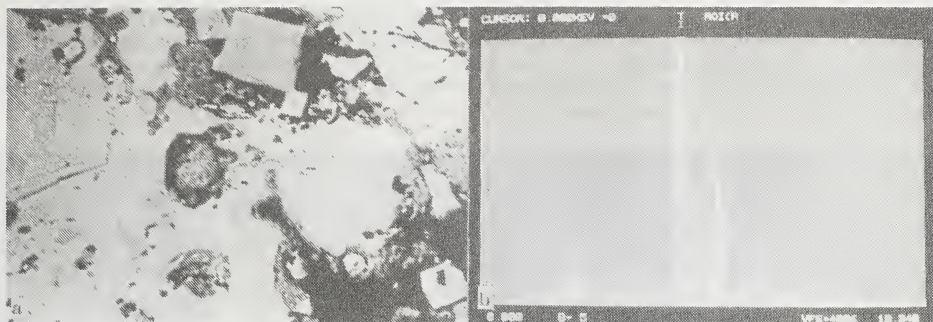


Fig. 1 (a) Backscattered electron image (composition) of crichtonite, illustrating the solid solution of mathiasite (dark grey) and loveringite (light grey); note the subhedral chromite which is a product of decomposition of crichtonite; (b) Energy dispersive spectrum of loveringite, showing higher CaO content

Cr-priderite intergrows with yiemengite. It differs in small cations from priderite $(K, Ba)_2(Ti, Fe)_6O_{13}$ which is described by Post (1982). The small cation position in Cr-priderite is dominated by titanium (65.02 wt % TiO_2), followed by chromium (14.23 wt % Cr_2O_3). Iron concentration is about 3.19 wt % FeO. The large cation position is dominated by potassium (5.91 wt % K_2O) and barium (8.52 wt % BaO). So Cr-priderite is distinguished also from priderite in Arkansas, United States.

Table 1

Representative analyses of Cr-priderite (PR-1, PR-2), yiemengite (YM-1, YM-2), mathiasite (MA-1), lindsleyite (LI-1), loveringite (LO-1) and chromite (CR-1).

All samples come from kimberlites in Shandong Province, China.

The analyses were done at the BRGM electron microprobe facility in France.

	PR-1	PR-2	YM-1	YM-2	CR-1	LI-1	MA-1	LO-1
K_2O	5.91	5.79	3.38	3.27	0.03	0.85	1.19	0.81
CaO	0.01	0.03	0.13	0.13	0.02	0.46	0.62	1.42
BaO	8.52	7.64	3.03	2.93	0.09	2.95	1.85	1.67
Na_2O	0.27	0.19	0.01	0.05	0.00	0.05	0.05	0.09
SrO	0.00	0.00	0.12	0.00	0.00	0.77	0.40	0.56
TiO_2	65.02	64.99	29.57	29.72	5.81	57.45	59.43	60.36
ZrO_2	0.00	0.00	0.04	0.00	0.00	4.26	4.79	4.65
Cr_2O_3	14.23	13.38	37.18	37.02	54.97	17.70	15.71	16.75
Al_2O_3	0.22	0.21	1.08	1.11	1.77	0.48	0.62	0.66
V_2O_5	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.26
FeO	3.19	3.21	17.77	17.85	25.07	8.05	9.36	7.48
MgO	0.50	0.47	5.69	5.72	10.73	3.76	4.08	4.02
MnO	0.04	0.06	0.22	0.19	0.35	0.02	0.14	0.13
Nb_2O_5	2.37	2.09	1.03	1.23	0.00	3.97	2.60	1.40
Tr_2O_3	-	-	-	-	-	1.00	1.00	1.00
Total	100.29	98.51	99.26	99.21	98.84	100.86	100.66	100.24

These LIL-bearing Ti-Cr-Fe oxides are also associated with several other highly incompatible element-rich phases: (1) Cr-bearing picroilmenite with Cr_2O_3 4-8 wt % and MgO 10-15 wt %; (2) Ti-bearing chromite with TiO_2 about 5 wt %; (3) Cr-bearing pyrope with Cr_2O_3 about 5-10 wt %; (4) Other rare minerals and unidentified mantle minerals.

This association of LIL-bearing oxides described here is indicative of a highly alkalic environment. Considering other LIL-bearing oxides discovered in Jagersfontein Kimberlites (Haggerty, 1983) and Western Australian leucite-lamproites, the role of alkalis in the mantle and the origin of alkalic rocks in general has thus taken on a new dimension. On the other hand, this association of LIL-bearing oxides is also enriched in refractory and incompatible elements. It shows clearly that these minerals precipitate in residual liquids during crystallisation or fractionate into liquids

during partial melting. In a word, these mineral chemistries are sufficiently diagnostic to warrant consideration for the existence of very specific conditions in some regions of the upper mantle. It is concluded that the refractory and LIL-bearing oxides association resulted from metasomatism by the introduction of liquids enriched in above elements into harzburgites or peridotites (Haggerty, 1983).

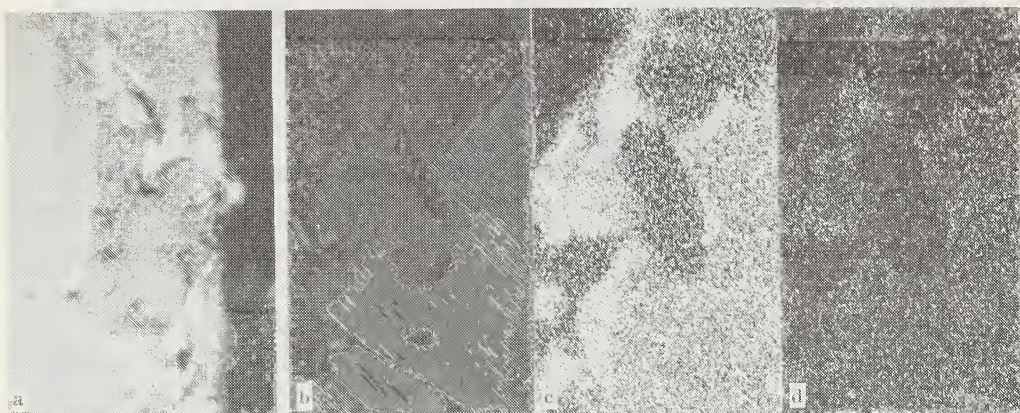


Fig. 2 (a) Reflected light photomicrograph taken under oil-immersion objectives, partial decomposition of yiemengite containing subcubic spinels (dark grey) and Cr-priderite (white) in the rim; (b) Backscattered electron image (composition); (c) Ti K X-ray image; (d) K K X-ray image. (b)-(d) in the same area, showing the intergrowth of yiemengite, chromite and Cr-priderite.

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