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Hydrothermal Mobility of Ti, Zr and REE: Examples from the Bergell and Adamello Contact Aureoles (Italy)

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ABSTRACT

Contact metamorphic marbles, affected by metasomatic fluids at the contact to the Bergell and Adamello Intrusives, contain various accessory minerals (zirconolite, allanite, titanite, rutile, geikielite, hoegbomite), which provide new evidence for the hydrothermal mobility of Ti and Zr. In both examples, Ti and Zr migrated along with U, Th, Y and REE in a metasomatic fluid rich in potassium. The composition of the main minerals (fluorine-rich phlogopite, pargasite and titanian clinohumite) and the abundance of fluor-apatite demonstrate that fluorine and phosphorus were important components of the fluid. The textural relationships indicate that the formation of the accessory phases is linked to the crystallization of the hydrous minerals.

INTRODUCTION

The rare earth elements (REE) and other trace elements such as titanium, zirconium and yttrium have long been considered to be immobile during metamorphism or alteration. In geochemical studies their abundance has commonly been used as a critical diagnostic tool to evaluate empirically the petrogenesis (by chondrite-normalized REE-patterns) and the tectonic setting (by the Ti–Zr–Y-discrimination diagrams of Pearce and Cann (1973) of basic volcanic rocks.

There is increasing evidence, however, that these elements, particularly the REE, may be transported by metamorphic fluids under a wide variety of geological conditions (e.g. Rudashevskiy, 1969; Rekharskiy and Rekharskaya, 1969; Sinyakov and Nepeina, 1969; Pavelescu and Pavelescu, 1972; Zhuravleva et al., 1976; Staatz et al., 1977; Graf, 1977; Hellman and Henderson, 1977; Van Wambeke, 1977; Konev, 1978; Martin et al., 1978; Hellman et al., 1979; Ludden and Thompson, 1979; Alderton et al., 1980; Dostal et al., 1980; Hynes, 1980; Taylor et al., 1981; Taylor and Fryer, 1980, 1983; Baker and De Groot, 1983; Nyström, 1984; Robins, 1984; Gieré, 1986; Cathelineau, 1987; Vocke et al., 1987). The occurrence of U-REE daughter crystals in fluid inclusions infers that the REE are present in high concentrations in certain hydrothermal fluids (Kwak and Abeysinghe, 1987). Similarly, titanite, anatase and rutile in fissures from the granitic massifs of the Swiss alps (e.g. Mercolli et al., 1984) indicate that titanium can be an important constituent of metamorphic fluids. Large amounts of Ti, Zr and REE have also been found in highly alkaline (pH = 12), fluorine-, silica- and sodium-rich groundwaters from the deep zones of the Lovozero alkaline massif (Kraynov et al., 1969).

This paper is a review of the current knowledge on the mobility of Ti, Zr and REE. It provides a description and comparison of two localities (Bergell and Adamello contact aureoles, Italy), where contact-metamorphic marbles have been affected by metasomatic fluids enriched in the high-valence cations of the above-mentioned elements. This type of metasomatism is restricted in both places to a rather narrow zone along the intrusive contact.

BERGELL

In the Bergell contact aureole (on the border between Switzerland and Italy) mobility of these elements has been inferred in a metasomatically altered spinel–calcite–marble occurring at the eastern margin of the Tertiary calc-alkaline intrusives. Geological setting and detailed mineralogy of the skarn were given by Gieré (1986). The mineralogy is briefly summarized here.

The contact metamorphic spinel–calcite–marble has been transformed by a metasomatic fluid into a coarse-grained skarn that consists mainly of fluorine-bearing phologopite, anorthite and partially altered spinel, with interstitial relics of calcite. Textural relationships indicate that the spinel has been altered in three consecutive steps to (1) hoegbomite (a complex Fe–Mg–Al–Ti-oxide) or corundum+magnetite, (2) margarite, and (3) chlorite. These relationships are illustrated in Fig. 1, where a spinel crystal is pseudomorphically replaced by corundum+magnetite, which was then overgrown by chlorite. Furthermore, the skarn contains large amounts of fluor-apatite as well as the accessory REE-bearing minerals zirconolite (ideally $CaZrTi_2O_7$), allanite and titanite, of which zirconolite is the most abundant.

The Bergell zirconolites exhibit three discrete growth zones, each possessing a distinctive chemical composition. Besides having markedly different yttrium and major element (Ca, Zr, Ti) contents, the three zones are clearly distinguishable on the basis of their characteristic REE patterns (for details see Williams and Gieré 1988).

Because of its ability to accommodate a large variety of elements, which range both in ionic radius and charge (30 or more elements with concentrations in excess of 0.1 wt%; see Wark et al., 1974), zirconolite provides important qualitative information on the availability of
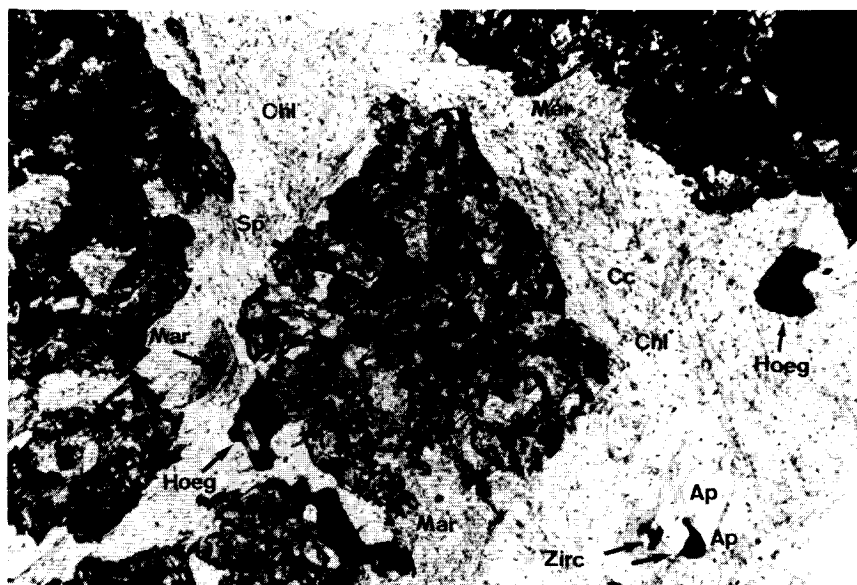
Fig. 1. *Photomicrograph of Bergell skarn, showing a spinel-pseudomorph consisting of corundum (high relief)+vermicular magnetite (opaque). The pseudomorph contains tiny relics of spinel (Sp, dark coloured) and is overgrown by chlorite (Chl) and margarite (Mar, lower left side of pseudomorph). Relics of hoegbomite (Hoeg) and margarite as well as zirconolite grains (Zirc) and fluor-apatite (Ap) are visible in chlorite. Cc = calcite. The largest diameter of pseudomorph is 0.7 mm.*
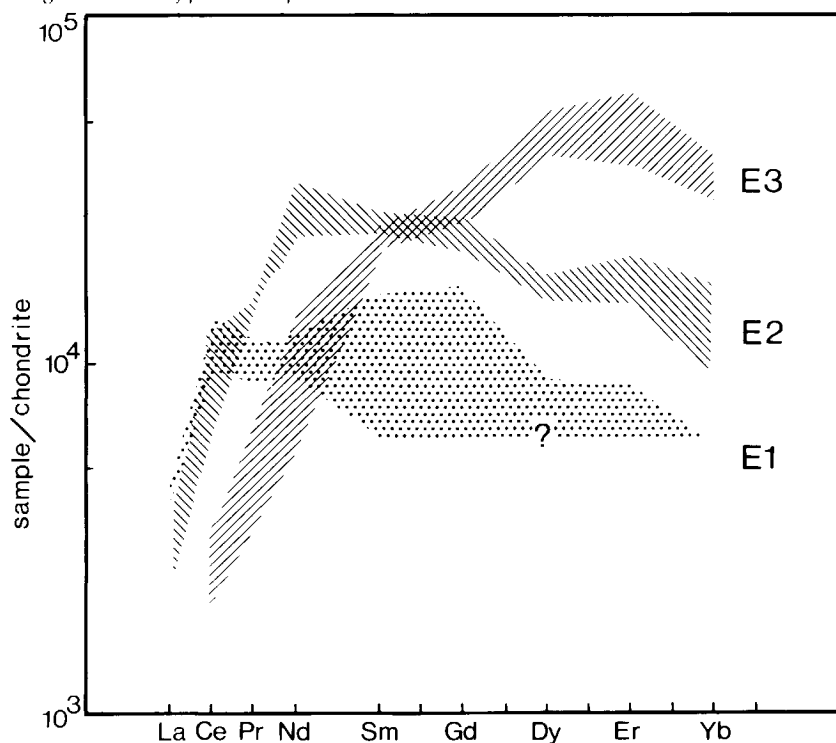

Fig. 2. *Chondrite-normalized REE plots (electron microprobe data) for the three zones of the metasomatic Bergell zirconolites. Zone E1 represents the core, zones E2 and E3 form rims around E1 and E2 respectively. The distinct REE patterns reflect a progressive, but stepwise evolution of the fluid from light to heavy REE enrichment during the three-stage alteration of the skarn. Shaded areas show range of values within each zone. Chondrite values after Wakita et al. (1971). Diagram from Williams and Gieré (1988).*

trace elements, particularly of REE, during its crystallization. In a metasomatic environment the zirconolite composition thus reflects the composition of the fluid.

The chondrite-normalized REE plots of the Bergell zirconolites (Fig. 2) indicate a progressive, but stepwise evolution of the fluid from light to heavy REE enrichment during crystallization from the inner (E1) to the outer (E2) zones. This three-stage crystallization seems to reflect the three-stage alteration of spinel. However, these two processes can only be linked to one another through one textural relationship observed in thin section; the crystallization of zirconolite zone E1 preceeds the third alteration stage, during which both the metasomatic phlogopite and the spinel have been chloritized (see Gieré 1986). This means that at least one zirconolite zone formed contemporaneously with phlogopite. It further leads to the suggestion that the metasomatic fluid transported *potassium* together with Ti, Zr, U, Th, W, Nb, Y and the REE (see Williams and Gieré 1988). The abundance of idiomorphic fluor-apatite and fluorine-bearing phlogopite, as well as their close association with the accessory minerals that incorporate these elements, point to F^- and PO_4^{3-} as likely ligands for complexing the above-mentioned elements in the fluid phase.

ADAMELLO

Similar metasomatism is also found at the contact between the Tertiary Adamello batholith (northern Italy) and the dolomitic country rocks.

Along the contact, the hornblende- and biotite-bearing tonalite of the southernmost Adamello pluton is altered to an assemblage of diopside and plagioclase, with minor titanite and calcite. The adjacent contact-metamorphic pure dolomite marbles are crosscut by dikes of altered tonalite and aplitic granite as well as by a complex system of different vein types. The mineral assemblages of one vein type indicate that a fluid containing Ti, Zr, REE and actinides was present during its formation.

This vein type is characterized by four mineralogically distinct zones, separated from each other by sharp boundaries. From the vein centre to the rim,

the following assemblages occur (see Fig. 3):

(1) titanian clinohumite + Vanadium-rich spinel+calcite+sulphides,
(2) phlogopite+calcite+titanite+sulphides,
(3) pargasite+calcite+titanite+sulphides,
(4) forsterite+calcite.

Titanium is a major element in the three central assemblages: this is demonstrated by (a) the occurrence of titanian clinohumite as a main constituent in one zone, (b) the abundance of titanite in the pargasite and phlogopite zones, and (c) the presence of various accessory Ti-minerals–zirconolite, geikielite (Mg-analogue of ilmenite),

rutile (see Fig. 3).

Two generations of zirconolite can be distinguished on the basis of their composition and crystal shape: in the titanian clinohumite zone, zirconolite is present as idiomorphic (Fig. 4), U- and Th-rich crystals with low REE contents [UO_2 = 11.7 wt%, ThO_2 = 6.9 wt%, ($REE_2O_3+Y_2O_3$) = 2.3 wt%], whereas, in the phlogopite zone it occurs as xenomorphic (Fig. 5) grains characterized by lower U and Th contents and generally higher, but variable REE concentrations [UO_2 = 2.2 wt%, ThO_2 = 3.5 wt%, ($REE_2O_3+Y_2O_3$) = 2.1–17.5 wt%; R. Gieré and C.T. Williams, in preparation].

Sulphides, mainly pyrrhotite and chalcopyrite, as well as idiomorphic fluor-apatite (Fig. 6), are found in all the Ti-rich vein zones. The main minerals in these zones are hydrous silicates (titanian clinohumite, pargasite, phlogopite) with high proportions of their OH^- groups substituted by F^- (R. Gieré, in preparation). No apatite has so far been found in the forsterite+calcite zone which does not contain any of the accessory phases rich in Ti, Zr, Y and REE.

Whole-rock Nd isotopic data for the three central zones show only little variation (ε_{Nd} = −2.1 to −2.5 at t = 40 Ma, i.e. time of intrusion); they are identical or close to the data for the unaltered hornblende–biotite–tonalite (ε_{Nd} = −2.5), but significantly different from those for the altered tonalite at the immediate contact with the dolomite marble (ε_{Nd} = −4.4, Gieré et al., 1988).

The preliminary Nd data indicate that the vein-forming fluid was isotopically different from the fluid involved in the above-mentioned alteration of the tonalite. The data also point to a Nd-isotope equilibrium between the fluid and the unaltered tonalite, which suggests that the veins have been generated during the emplacement of the tonalite (Gieré et al., 1988). A syn-intrusive formation of the veins is also implied by the field relationships.

The differences in composition of zirconolite in the phlogopite and the titanian clinohumite zones most probably reflect a change in trace element content of the metasomatic fluid. Xenomorphism and compositional variability of zirconolite within the phlogopite zone might be due to partial dissolution and
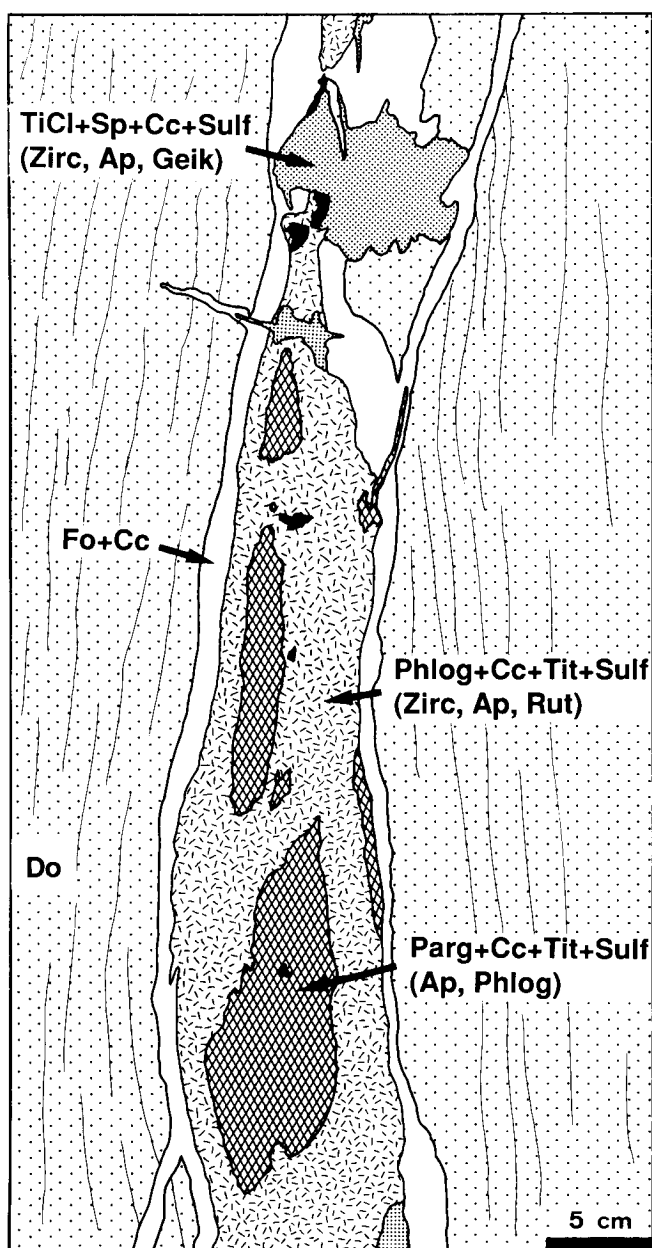

Fig. 3. *Mineralogical map of a Ti- and Zr-rich vein in contact metamorphic dolomite marble (Do) from the Adamello contact aureole.* Fo = *forsterite*, TiCl = *titanian clinohumite*, Phlog = *phlogopite*, Parg = *pargasite*, Sp = *spinel*, Cc = *calcite*, Tit = *titanite*, Sulf = *sulphides*, Rut = *rutile*, Ap = *apatite*, Zirc = *zirconolite*, Geik = *geikielite*. *Black areas represent large aggregates of sulphides (pyrrhotite, chalcopyrite)*
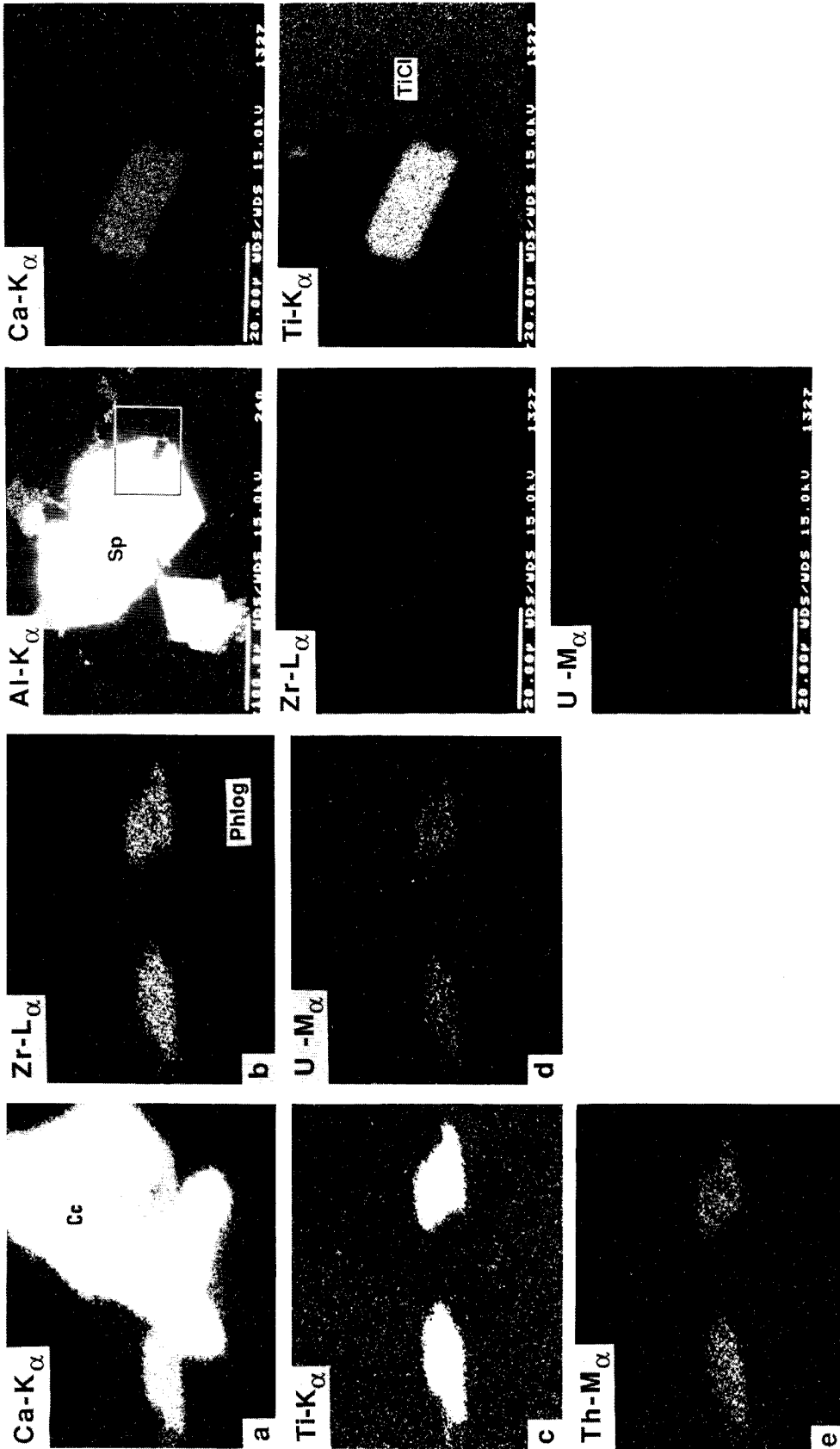
Fig. 4. Characteristic X-ray distribution pictures of Al, Ca, Zr, Ti, and U, showing an idiomorphic zirconolite crystal enclosed in spinel (Sp) from the titanian clinohumite (TiCl) zone, Adamello veins (see Fig. 3). Electron microprobe analytical conditions were 15 kV and 20 nA measured on a Faraday cage (Cameca SX-50).

Fig. 5. Characteristic X-ray distribution pictures of Ca, Zr, Ti, U and Th, showing xenomorphic zirconolite crystals in contact with phlogopite (Phlog) and calcite (Cc), phlogopite zone of the Adamello veins (see Fig. 3). Largest diameter of the zirconolite grains is 0.012 mm (left) and 0.01 mm (right). Electron microprobe analytical conditions were 15 kV and 20 nA measured on brass (ARL-SEMQ).
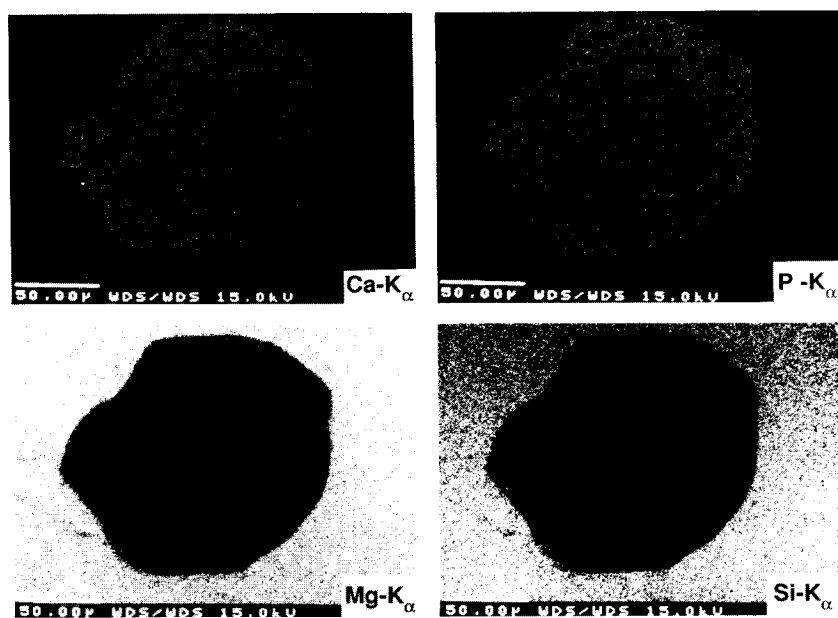
Fig. 6. *Characteristic X-ray distribution pictures of Ca, P, Mg and Si, showing an idiomorphic fluor-apatite crystal enclosed in titanian clinohumite from the central zone, Adamello veins (see Fig. 3). Electron microprobe analytical conditions were 15 kV and 20 nA measured on a Faraday cage (Cameca SX-50).*

leaching by the fluid at a later stage of vein formation (i.e. during the generation of the titanian clinohumite zone).

The high F-contents of titanian clinohumite, pargasite and phlogopite, as well as the abundance of fluor-apatite, indicate that fluorine and phosphorus were important components of the metasomatic fluid during the formation of the three Ti-, Zr- and REE-rich mineral zones. The origin and significance of sulphur in the veins is not yet understood on the basis of the currently available data.

DISCUSSION

The examples from the Bergell and the Adamello contact aureoles provide new evidence for migration of elements that commonly are regarded as immobile. In both cases, these elements mainly comprise Ti, Zr, U, Th, REE and Y, all of which are characterized by a high-valent ionic state.

Many studies show that these elements, particularly the REE, are mobile under a wide variety of physical and chemical conditions (references cited earlier). Unfortunately, there are very few experimental studies on the be-

haviour of these elements in fluids, and most of them deal with the REE only. Consequently, little is known about the processes responsible for (1) their mobilization by the fluid in the source area, (2) their transport in the fluid, and (3) their deposition as metasomatic minerals in veins or skarns.

Mobilization

Mobilization of these trace elements can be caused either by separation of a fluid phase from the melt in magmatic environments or by alteration processes (e.g. dissolution, leaching) involving magmatic, metamorphic or meteoric fluids. This is indicated by experimental investigations on the partitioning of REE between vapour and melt and between vapour and crystals; the experiments demonstrate that the extent of REE partitioning into the fluid is strongly dependent on pressure and temperature as well as on melt, crystal and fluid composition (Cullers et al., 1973; Balashov and Krigman, 1975; Flynn and Burnham, 1978; Mysen, 1979; Wendlandt and Harrison, 1979).

It is difficult to determine the characteristics of the environment where the

fluid was enriched in the trace elements of interest: important information, however, can be provided by isotope data. In the Adamello example, the Nd data suggest that the vein-forming fluid was in Nd-isotope equilibrium with the unaltered tonalite. Furthermore, the carbon and oxygen isotope data for the pure dolomite marble, the vein calcite (from all mineral zones) and the tonalite (see Fig. 7) point to a fluid that has been derived from the tonalite and diluted by wall rock (dolomite) components. These results indicate a magmatic (tonalitic) origin of the vein-forming fluid, and suggest that the trace elements were fractionated into the fluid during its separation from the melt, and not during the alteration of the tonalite which was caused by a fluid from a different source.

Transport

The nature and activity of dissolved anionic or molecular species in the fluid play an important role not only during the mobilization of these metals, but also during their transport. Although few data are available, it has been demonstrated both empirically (in field studies, references cited) and experimentally (Kosterin, 1959; Balashov and Krigman, 1975; Flynn and Burnham, 1978; Bilal and Becker, 1979; Bilal et al., 1979; Bilal and Koss, 1980a,b; Nguyen, 1985), that the anions F^-, Cl^-, OH^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} can be effective ligands for complexing REE and U. Mobility of Ti and Zr seems to be favoured by relatively high activities of CO_2 (Hynes, 1980), B^- (Alderton et al., 1980; Konev, 1978) or F^- and PO_4^{3-} (Kraynov et al., 1969; Gieré, 1986) in metasomatic fluids; they also migrate in surface waters at ambient temperatures and pressures, mainly because of complex formation with humic and fulvic acids (e.g. Samchuk and Sushchik, 1986). Furthermore, the mineralogy of many Ti- and Zr-rich skarns or veins suggests that these metals migrated in those cases along with *potassium* and/or *sodium* (e.g. Moleva and Myasnikov, 1952; Semenov et al., 1963; Mineyev, 1963; Zhuravleva et al., 1976; Konev, 1978), possibly as *mixed-metal polynuclear complexes* with K^+ or Na^+ (see also Bandurkin 1961). However, veins that contain titanian hydroxyl-clinohumite,

perovskite and hydroxyl-apatite from the Malenco serpentinites, northern Italy (Trommsdorff and Evans, 1980) demonstrate that the transport of titanium is *not* restricted to fluids rich in potassium or fluorine.

A more direct inference on fluid compositions can be drawn either from the analysis of ground waters and waters from active hydrothermal systems (e.g. Kraynov *et al.*, 1969) or from analysis of fluid inclusions in vein or skarn minerals; Kwak and Abbeysinghe (1987), for example, demonstrated in their fluid inclusion study that a high-temperature (550–670°C), saline (30–70 wt% total dissolved salts, mainly $CaCl_2$) and oxydizing ore solution was able to transport large quantities of REE and U.

Unfortunately, no fluid inclusions suitable for analysis have been found in the Bergell or the Adamello rocks. However, the composition of the main minerals (including fluor-apatite) implies relatively high activites of fluorine, phosphorus and potassium (in what-ever speciation) in the metasomatic fluid during formation of the skarn (Bergell) and the mineral zones rich in Ti, Zr, U, Th, Y and REE (Adamello). Furthermore, the occurrence of abundant sulphides (Adamello only) and calcite indicates the presence of sulphur and CO_2 as well. A more quantitative approach to determining the fluid composition is currently underway by applying experimentally determined fluid/mineral exchange equilibria to some Adamello vein minerals.

Deposition

The deposition of these trace elements as metasomatic minerals is closely linked to changes in temperature and fluid composition. Both an increase in salinity of the fluid, due to its reaction with the wall rock (e.g. Kwak and Abeysinghe 1987), or a temperature decrease in space or time could cause supersaturation with respect to less soluble compounds (e.g. complexes with high-valence cations), resulting in their precipitation.

However, in the Bergell and Adamello examples, the textural relationships observed in thin section indicate a different cause for precipitation of the trace elements: a decrease in ligand activity of the fluid due to crystallization of hydrous minerals. The latter (Bergell: phlogopite, apatite; Adamello: phlogopite, pargasite, titanian clinohumite, apatite) are generally idiomorphic (see Fig. 6) and closely associated with the accessory phases that incorporate the high-valence cations. Similar textural relationships have also been reported from other localities (Moleva and Myashnikov, 1952; Semenov *et al.*, 1963; Zhuravleva *et al.*, 1976; Konev, 1978), and support the hypothesis of trace element deposition caused by a lowering of ligand activity due to crystallization of hydrous minerals (including apatite).

A better understanding of these processes is not only required for a petrogenetic interpretation of veins and skarns rich in these metals, but also for the exploration of their economically important ore deposits. Mobilization of radioactive elements, in particular, is one of the main concerns in evaluating possible disposal options for high-level nuclear waste. Currently, the most promising form for immobilization of radioactive waste is a synthetic titanate ceramic (SYNROC-C), in which zirconolite is the principal host for Zr and tetravalent actinides as well as one of the most resistant phases with respect to hydrothermal leaching (e.g. Ringwood and Kelly, 1986). Detailed petrographic studies and determination of the composition of metasomatic fluids that coexisted with naturally occurring zirconolite may provide further information on the leaching behaviour of zirconolite in ceramic waste forms.
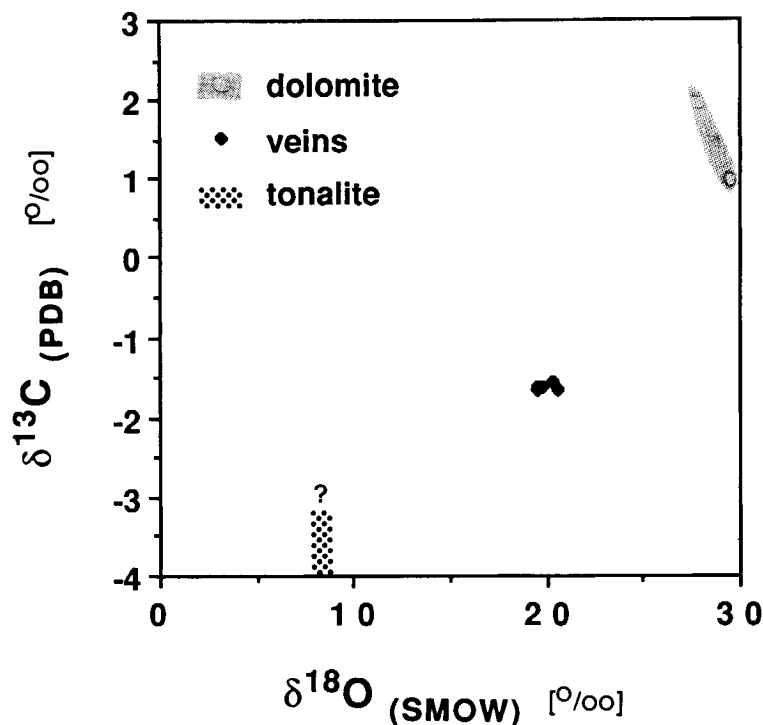
CONCLUSIONS

The following conclusions can be drawn from the comparison of the Bergell skarn and the Adamello veins.

(1) In both examples Ti and Zr migrated in the metasomatic fluid along with U, Th, Y and REE.
(2) Potassium was an important constituent of the metasomatic fluid transporting the high-valence cations (in the

Fig. 7. $\delta^{13}C$ vs. $\delta^{18}O$ *diagram for the Adamello samples. The dolomite field represents the range of values for the pure, dolomite marble wall rock unaffected by metasomatism. The $\delta^{13}C$ and $\delta^{18}O$ values for calcite from all four vein zones (see Fig. 3) show only little variation and are markedly lower than all data for dolomite. The tonalite field represents the whole rock $\delta^{18}O$ data only (no values for $\delta^{13}C$ for tonalite because of its very low carbon contents).*

Adamello at least during two stages of vein formation).

(3) The Nd isotopic data (Adamello) suggest a magmatic origin of the REE and, in combination with oxygen and carbon isotope data, of the fluid itself.

(4) The composition of the main minerals (including apatite) suggest F^- and PO_4^{3-} to be the most likely ligands for complexing of the high-valencece cations.

(5) Deposition of the trace elements is probably induced by the lowering of ligand activity in the fluid, resulting from crystallization of the hydrous minerals.

(6) Ti, Zr and REE are mobile under certain geological conditions, and therefore, extreme caution is needed in the interpretation of *altered* rocks on the basis of their trace element contents and proportions only.

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