

Rare earth and uranium minerals present as daughter crystals in fluid inclusions, Mary Kathleen U-*REE* skarn, Queensland, Australia

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Abstract

At least six separate rare earth and uranium-bearing daughter crystals occur in fluid inclusions hosted by andraditic garnet from the Mary Kathleen *REE*-U ore skarn, Queensland, Australia. The daughter minerals are particularly high in La, Nd and Ce which reflects the relatively high concentration of these in the bulk ore ($\text{La}_2\text{O}_3 = 33.5\%$, $\text{Nd}_2\text{O}_3 = 9.1\%$ and $\text{Ce}_2\text{O}_2 = 51.5\%$ of the 2.6 wt. % *REE* common in the ore). The host garnets themselves contain up to 7600 ppm *REE* and 5 to 2700 ppm U. The energy-dispersive spectra (EDS) are consistent with the following minerals: a (Y, Ce, U, Ca, Fe, Nb, Ta) mineral; a (Ca, Fe, Ce) carbonate(?) mineral; a (Fe, Ca, Y, Ce, Nb, Ta) mineral; a possible carbonate of La, Mn and Nd; a chlorite of Mn and La as well as a possible chloride or oxychloride of K, Mg, Mn and La. Their occurrence infers that relatively high concentrations of *REE* and U prevailed in the original, oxidized, concentrated (30–70 wt. % total dissolved salts), high-temperature (550–670°) ore solutions. Their presence as daughter crystals may be due to the fact that CaCl_2 is a dominant salt in the solutions and that the latter's solubility was sufficiently high to 'salt out' the less soluble *REE*-U components.

KEYWORDS: fluid inclusions, rare earth minerals, uranium, skarn, Queensland, Australia

Introduction

THE concentration of *REE* and U in high-temperature, saline ore fluids responsible for the genesis of pegmatites, certain greisenized granites and some ore skarns is poorly known. Leachate analyses for these have rarely been carried out, although Rankin *et al.* (1982) tentatively report concentrations of 200–300 ppm U from fluid inclusions in quartz. The occurrence of *REE*- and U-bearing daughter crystals have also rarely been reported. Brown (1983) has inferred that a mineral of the bastnäsite group $[(\text{La,Ce})\text{FCO}_3]$ occurs in fluid inclusions in quartz from the Hole 16 deposit, Queensland, Australia. Roedder (1984, p. 390) has predicted that such minerals should occur as daughter minerals, particularly in fluid inclusions in complex pegmatites. However, although up to 16

daughter crystals have been found in some fluid inclusions (e.g. Volynia, U.S.S.R. in Roedder, 1984, p. 392), none of these have proved to be *REE*- or U-bearing.

Skarns offer a special geochemical environment for ore deposition because the reaction of ore solutions with carbonate represents an ideal geochemical 'trap' to concentrate metals. Iron, the major component added to any ore skarn, is generally transported as a chloride such as FeCl_2 and, during skarn genesis, large amounts of CaCl_2 are produced to maintain chemical equilibrium in the system (see Kwak and Tan, 1981). Salts having divalent cations such as CaCl_2 , MgCl_2 , FeCl_2 , ZnCl_2 , etc. are generally more soluble than those having univalent cations, such as KCl and NaCl. CaCl_2 is one of the most soluble salts found in hydrothermal systems. If substantial quantities of

such a salt are added to a saturated aqueous solution containing less-soluble salts, the total salinity generally increases and, if enough of the more soluble salt is added, quantities of the less-soluble salts precipitate on supersaturation. For example, a saturated $\text{NaCl} + \text{KCl} + \text{H}_2\text{O}$ solution contains 20.42 and 11.14 g/l NaCl and KCl respectively at 28 °C while a saturated $\text{CaCl}_2 + \text{NaCl} + \text{KCl} + \text{H}_2\text{O}$ solution contains 44.8, 0.6 and 3.2 g/l CaCl_2 , NaCl and KCl respectively (Linke, 1965). The total salinity is higher in the latter case (48.6 versus 31.56 g/l) while the quantities of KCl and NaCl are much reduced. Thus if excess CaCl_2 were added to a saturated $\text{KCl} + \text{NaCl} + \text{H}_2\text{O}$ solution then, if the quantity of water present remains constant, 44.8 g/l of CaCl_2 would be dissolved and 19.82 and 8.2 g/l of NaCl and KCl respectively will precipitate as solids or be 'salted out' when equilibrium is reached.

As the genesis of ore skarn also involves the genesis of substantial quantities of CaCl_2 , reacted or 'exhaust' ore solutions are ideal for producing large and distinctive daughter assemblages if dilution by meteoric water does not occur. Because of this mechanism, daughter crystals in ore skarn minerals can be expected to differ from those in most other ore environments.

Ore skarns in which large amounts of *REE* and *U* occur are rare, although lesser amounts of these elements are probably common in many skarns. The economic Mary Kathleen *U*-deposit and the nearby Rita and Elaine Dorothy skarns, Queensland, Australia, represent some of the few examples of such skarns and have been the subject of a great deal of study by the authors (Abeyasinghe, 1985; Abeyasinghe *et al.*, 1984; Abeyasinghe and Kwak, 1985). The deposits are true 'ore' skarns (see Einaudi *et al.*, 1981, for discussion) and formed by the reactions of externally derived *Fe-REE-U*-bearing solutions with carbonate, initially at near-magmatic conditions. The Mary Kathleen deposit alone is a huge potential *REE* resource. The deposit contains about 6 million tonnes of ore at 0.1% U_3O_8 and 2.6% *REE*. The main *REE* present in percentage are: La (33.5%), Ce (51.5%), Pr (4.0%), Nd (9.1%), Sm (1.1%) and Th (0.64%).

The objectives of the study are to identify uranium and rare-earth-bearing daughter minerals and to discuss the significance of high *REE* and *U* solubilities contained in these high CaCl_2 -bearing solutions.

Geological setting and mineralogical characteristics of the Mary Kathleen skarn

The Mary Kathleen and the nearby smaller Rita and Elaine Dorothy skarn deposits occur in

Northern Queensland, Australia (20° 45' S, 140° 1' E), within a metamorphosed sedimentary sequence marginal to a number of igneous rock types. The source of the ore solutions is most probably the Burstall granite and related porphyry dykes (e.g. Derrick, 1977; Abeyasinghe *et al.*, 1984) with the major conduits for ore solution flow being the dykes or dyke margins and the Mary Kathleen shear (Abeyasinghe and Kwak, 1985). As in many ore skarn deposits, there is a sequential relationship of mineral assemblages as follows: early andradite garnet + quartz + diopside-hedenbergite pyroxene + scapolite (Stage 1), followed by ferrohastingsite + sulphides or *REE*-allanite + stillwellite + uraninite + apatite (Stage 2) and finally sulphides + chlorite + prehnite + calcite (Stage 3). Stage 2 has replaced Stage 1 minerals with the ferrohastingsite-bearing assemblage generally occurring at depths below the allanite-bearing assemblage, which constitutes the ore mined. The uranium is found mainly as uraninite, while the *REE* occur mainly in allanite with totals near to 20 wt. % (to 10.75% Ce_2O_3 , 8.68% La_2O_3 and Nd, 1.80%) as well as volumetrically minor stillwellite (*REE,Ca*) BSiO_5 . The fluid inclusions which contained the *REE*- and *U*-bearing daughter crystals reported here are all found within the Stage 1 andradite-rich garnet (And_{54-95}). Garnet itself contains only trace amount of *REE* (0.06 to 0.76 wt. %), mainly Ce and La, although one individual probe analysis of 3.66 wt. % La_2O_3 , 4.20% Ca_2O_3 and 0.63% Nd_3O_4 was found. Uranium values as determined by electron microprobe analysis are equally low in garnet, often being below the detection limit (0.04 wt. %), although values as high as 0.27 wt. % were found. Uranium was also detected in garnet using fission track counting methods and found to be greater than 5 ppm and often much higher; the fission track densities were zonal, and reflect the growth zones of the garnet. Fission track densities within individual growth zones were generally constant. It is thus apparent that the garnet grew in, or formed from a solution which contained *REE-U* aqueous species in anomalous amounts.

Fluid inclusion characteristics

Two types of primary fluid inclusions occur in ore garnet namely (a) saline ones containing one or more, and commonly three to four daughter crystals, with small gas bubbles, and (b) dilute ones in which large gas bubbles occur. These were generally only up to 30 μm in their longest dimension (Fig. 1), making the extraction of the much smaller daughter crystals impossible. First-melting

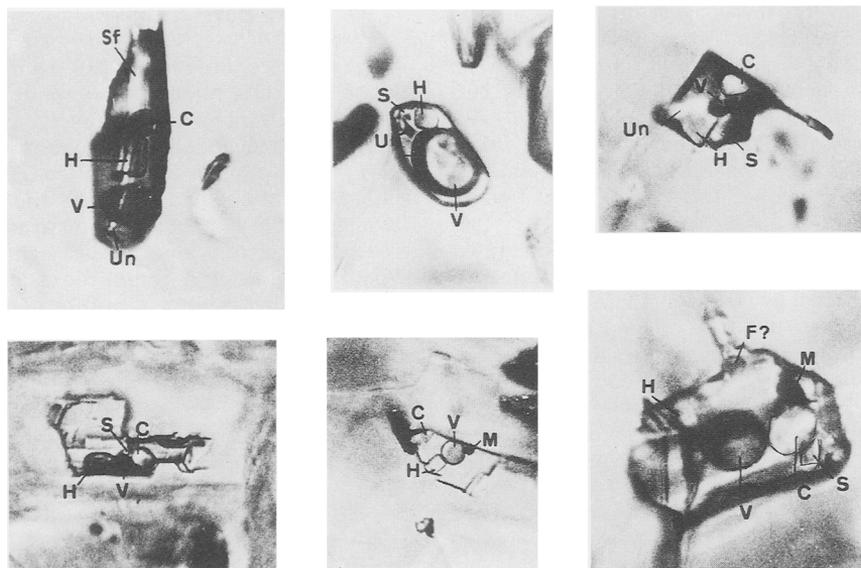


FIG. 1. Typical fluid inclusions in garnet. V = vapour phase, H = halite, S = sylvite, C = calcium chloride, F = fluorite, M = magnetite, Un = unknown, Sf = saline fluid. The fluid inclusions are from approximately 10 to 20 μm long.

temperatures (T_{eutectic}) are mainly in the range -60 to -50 $^{\circ}\text{C}$ with fewer in the range -65 to -60 $^{\circ}\text{C}$ and few in both the -80 to -75 $^{\circ}\text{C}$ and -45 to -40 $^{\circ}\text{C}$ ranges.

The solutions represented by the primary fluid inclusions were inferred to be dominantly $\text{CaCl}_2 + \text{KCl} + \text{NaCl} - \text{H}_2\text{O}$ as deduced from: (1) the identification of halite, sylvite and antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) daughter crystals using scanning electron microscope analysis (energy-dispersive spectrometry) and optical observations; (2) volumetric measurements of the fluid inclusion constituents combined with published solubility data on salt- H_2O systems (in Linke, 1965). Liquid CO_2 was an extremely rare constituent. A typical calculated fluid composition in weight percent is as follows:

H_2O , 45.3; NaCl , 6.8; KCl , 7.8; CaCl_2 , 34.8; Fe_3O_4 , 2.1 (magnetite was often present) and unknown solid species, 3.2 with a total salinity of 54.7 wt. % total dissolved salts.

Salinities ranged from 32 to 72.8 wt. % total dissolved salts with most being in the 40 to 60 wt. % range. Fluid inclusion filling temperatures varied from approximately 300 up to 800 $^{\circ}\text{C}$ (inferred beyond 700 $^{\circ}\text{C}$) with many in the 550 to 670 $^{\circ}\text{C}$ interval.

Daughter crystal identification method

The identification of the daughter minerals reported here involved both optical and SEM techniques. The limitations of optical methods to elucidate the identification of the often minute daughter crystals is well known. The use of a scanning electron microscope coupled with an X-ray detector for the qualitative identification of daughter minerals in opened fluid inclusions has been demonstrated by Metzger *et al.* (1977). This method has been successfully used by other workers (Kwak and Tan, 1981a; Ypma and Fuzikawa, 1980).

Drill core samples were crushed and mineral fragments with freshly broken surfaces were selected. These were further broken along cleavage planes where possible, using a very small chisel. The fragments were mounted on glass slides and coated with electrically conductive carbon paint. Only the freshly broken surfaces of the mineral fragments were examined. After mounting, the samples were stored in a desiccator because some daughter crystals are unstable in air e.g. hydrated iron chlorides are deliquescent (Weast, 1974). Storage in a vacuum is unsuitable as some hydrated salts may be efflorescent e.g. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ breaks down to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Mellor, 1928).

A Jeol scanning electron microscope (model JSM

35) with an energy-dispersive X-ray analyser (EDS) system using a silicon crystal detector was used in this study. Experimental conditions were: accelerating potential, 20–30 kV; objective lens aperture, 200 μm ; and working distance, 39 mm. Count times of 100 seconds were used in all cases. An electron beam diameter of approximately 100 \AA was standard and gave a resolution of 100–200 \AA .

The primary electron beam often penetrated through the commonly small daughter minerals (ranging from 0.2 to 3.0 μm in diameter, average = 0.6 μm) and into the host mineral producing an X-ray spectrum which was the result of contributions from both the host and the daughter mineral. Although penetration depth is a function of accelerating voltage, a poor image results at lower accelerating voltages and, consequently, higher voltages were chosen.

Daughter minerals

The solid crystals present are assumed to be daughter crystals rather than captured mineral phases because none of the mineral species are represented as identified minerals elsewhere in the deposit. The positive identification of elements lighter than atomic number 11 by EDS analyses was not possible with the apparatus available. This restricted the identification of such light elements. Also, the daughter crystals were too small for X-ray diffraction. Where a large proportion or even all the elements present in a mineral are light, such as in $\text{Li}_2\text{B}_4\text{O}_7$ (Zolensky and Bodnar, 1982), more definitive tests such as X-ray diffraction are essential to produce an unequivocal identification. This was not possible for the samples analysed here and the results are restricted in this way.

The following daughter crystal minerals have

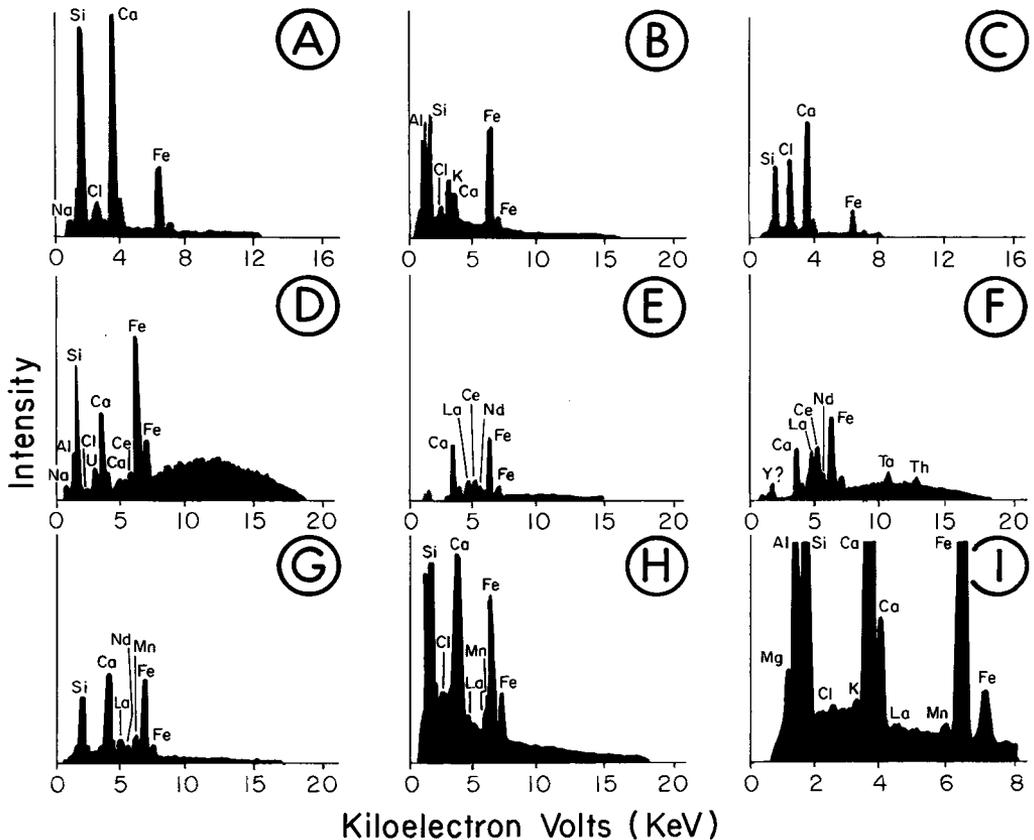


FIG. 2. Energy-dispersive spectra. A = halite, B = sylvite, C = antarcticite, D = U-bearing mineral, E = REE mineral, F = REE and Ta mineral, G = La-Mn mineral, carbonate (?), H = La-Mn-Cl minerals, I = K-Mn-Mg-La-Cl mineral.

been either identified or inferred based partly on SEM and partly on optical properties: halite, NaCl; sylvite, KCl; antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$); fluorite, CaF_2 ; calcite CaCO_3 ; ankerite $\text{Ca}(\text{Mg}, \text{Fe}, \text{Mn})(\text{CO}_3)_2$; magnetite, Fe_3O_4 ; samarskite (?), $(\text{Y}, \text{Ce}, \text{U}, \text{Ca}, \text{Fe})(\text{Nb}, \text{Ta})_2\text{O}_6$; sitaparite (?) $4\text{Mn}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3$; codazzite (?) $(\text{Ca}, \text{Fe}, \text{Ce})\text{CO}_3$; yttrantalite (?) $(\text{Fe}, \text{Ca})(\text{Y}, \text{Er}, \text{Ce}, \text{etc.})(\text{Ta}, \text{Nb})_4\text{O}_{15} \cdot 4\text{H}_2\text{O}$; a possible carbonate of La, Mn and Nd; a chloride of Mn and La; and a chloride or oxychloride of K, Mn, Mg and La. A detailed discussion concerning the identification and distribution of the non-REE-bearing daughter crystals found at Mary Kathleen is given elsewhere (Abeysinghe, 1985).

The EDS spectra are particularly definitive where the composition of the daughter minerals and those of the host do not overlap. Thus halite (NaCl) and sylvite (KCl) give separate peaks to that of the host garnet (Fig. 2A and B). Antarcticite occurs as long to stubby tabular crystals or as irregular grains and has definitive Cl peaks as well as enhancing the Ca peak of the host garnet on the spectrum (Fig. 2C). Equally, magnetite enhanced the Fe peak of the spectra of garnet, had no S peak and was suspected by its magnetism. The identification of fluorite, calcite and ankerite was less definitive, involving the interrelation between optics, the crystal form as determined by SEM studies and the EDS spectra.

The unusual REE- and U-bearing minerals are mainly determined by use of the EDS spectra rather than optical properties. The latter are either not sufficiently definitive or are unknown.

Uranium mineral. In a number of fluid inclusions dark brown, birefringent, elongate to stubby crystals occur having very high relief. A uranium-bearing daughter crystal was found having peaks for Ca, Si, Al, U, Ce, Na and Cl with a broad peak indicating a highly excited region of the spectra attributed to the occurrence of metallic elements (Fig. 2D). The anomalous peaks in the 7 to 16 keV region do not occur in the adjacent host mineral. When this region is expanded, minor peaks are apparent for Ta and Nb. The Na and Cl peaks in the spectrum are probably due to a neighbouring halite crystal. The mineral may well be a U-Ce oxide such as samarskite $(\text{Ce}, \text{U}, \text{Fe}, \text{Ca})(\text{Nb}, \text{Ta})_2\text{O}_6$, although a similar but perhaps up to now unknown mineral is also a possibility.

Rare earth mineral. The spectrum of a mineral having Ca, Fe, La, Nd and Ce peaks occurs in which no Si peak was observed (Fig. 2E). The lack of a Si peak shows the spectrum of the host garnet was not present while the lack of any anion species such as chlorine implies it is a carbonate, oxide, etc. species. The composition could fit the carbonate

codazzite $(\text{Ca}, \text{Fe}, \text{Ce}, \text{La}, \text{Nd})\text{CO}_3$, although the possibility that it is an equivalent mineral to, for example, bastnäsite $(\text{Ce}, \text{La})(\text{CO}_3)\text{F}$ cannot be ruled out, particularly if Ca and Fe substitution were possible for Ce and La.

Rare earth mineral. Another REE-bearing daughter crystal found in fluid inclusions contains Fe, Nd, Ca, Ce, Th, Y and Ta peaks (Fig. 2F). The minor peaks of Si and Al here are considered to be due to the host garnet. The possible mineral closest to this is yttrantalite $(\text{Fe}, \text{Ca})(\text{Y}, \text{Er}, \text{Ce}, \text{etc.})(\text{Ta}, \text{Nb})_4\text{O}_{15} \cdot 4\text{H}_2\text{O}$. Er and Nb were not detected however. Like the uranium mineral, a very broad peak occurs and minor Nb contents are possible which is marked by the peak.

A number of other REE daughter minerals occur which were generally of small size, with the result that the garnet spectrum is prominent. Consequently, it was not possible to infer whether Ca, Al, Fe or Si were present in the daughter minerals themselves. The following occur: (a) La-Mn-Cl (Fig. 2G), (b) K-Mn-Mg-La-Cl (Fig. 2H), and (c) Mn-La-Nd (Fig. 2I). Whether mineral (a) is a simple (AX_3) -type halide such as $(\text{La}, \text{Mn})\text{Cl}_3$ with trivalent Mn or a more complex oxyhalide type, such as a La-bearing kempite $(\text{Mn}_9\text{O}_6\text{Cl}_2 \cdot 3\text{H}_2\text{O})$, is not known. Mineral (b) is most likely a complex salt of the $A_m B_n X_p$ type where $(m+n):p > 1:2$. A La- and Mg-equivalent to chloromanganokalite $(\text{K}_4\text{MnCl}_6)$ is possible. Mineral (c) could be any of a number of mineral types including carbonate, fluoride, oxide or hydroxide.

Conclusions

It is unfortunate that the size of the daughter crystals was much too small to enable them to be extracted and for X-ray diffraction patterns to be made. In the absence of X-ray data and the identification of elements lighter than sodium, determination of the daughter crystals species is only tentative. However, the following conclusions can be drawn. (a) Unusual REE and U minerals occur as daughter crystals. These included at least six separate types, some of which are chloride-bearing, (b) Many of the constituent elements within these daughter minerals either do not occur in the garnet host (e.g. K) or occur in relatively low abundances (e.g. Mn, La, Ce, U, Nd) although Ca and Fe occur as well. None of the daughter crystals could be shown to be silicates.

These conclusions are compatible with the view that these solutions represent largely reacted or 'exhaust' ones, produced as a result of ore solution interaction with carbonate to produce skarn. This is apparent from the extremely high CaCl_2 contents present which can be shown to be produced during

skarn genesis (see Kwak and Tan, 1981). The *REE*- and U-bearing mineral species allanite, uraninite and stillwellite which occur in the skarn obviously postdate the crystallization of the garnet which hosts the fluid inclusions. The *REE* and U thus tend to remain in solution during early skarn genesis. It is notable that, like the *REE*:U ratio in the skarn (i.e. 2.6:0.1), *REE*-bearing daughter crystals are much more abundant. It is likely that *REE* and to a much lesser extent U must be very soluble in saline, high-temperature solutions at the relatively high f_{O_2} values at which andradite garnet (+ pyroxene) form. The probable reason *REE* daughter crystals have not previously been reported is that no solutions have been studied in which either *REE* concentrations were sufficiently high so as to be supersaturated on falling temperatures or there was no extremely soluble salt present such as $CaCl_2$ to 'salt out' such components. As no mineral having appreciable *REE* and U crystallized at this period of the skarn's evolution, the elements stayed in solution rather than precipitating as *REE*-allanite, uraninite and stillwellite as they did at a later time. The occurrence of the unusual daughter minerals in fluid inclusions in the Mary Kathleen skarn may thus reflect the unique environment of this type of mineralization.

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