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Bernhard Schulz · Steffen Hagemann ·  
Axel Gerdes · Jörg Pfänder

# Archean Rare-Metal Pegmatites in Zimbabwe and Western Australia

## Geology and Metallogeny of Pollucite Mineralisations

EXTRAS ONLINE

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# Preface

Lithium–cesium–tantalum (LCT) pegmatites are important resources for rare metals, whose demand increased markedly during the past decade. Especially, cesium and its compounds are used in drilling fluid in hydrocarbon exploration, as a catalyst in the chemical industry, and in advanced technology applications as atomic clocks, airbag detonators, high-resolution display screens or as a propellant agent in ion engines. The Cs metal market is actually in the frame of lower tens of thousand kilograms per annum. Data on resources and production are very limited. Cs resources can be categorised into one group of potassium salts, sedimentary rocks and seawater, all with no commercial interest due to low concentrations. The Cs resource group of commercial importance is LCT pegmatites that contain the rare zeolite group cesium mineral pollucite. At present, Cs and reserves of it are known in economic and mineable quantities only from the two LCT pegmatite deposits at Bikita in the Zimbabwe Craton and Tanco in the Superior Craton in Canada, where pollucite occurs in monomineralic mineralisation. Both pegmatite deposits have a comparable regional geological background, as they are hosted within greenstone belts and yielded Neo-Archean ages at  $\sim 2625$  Ma. A closure of the Tanco Mine for safety reasons and an imminent depletion of the pollucite resources at Bikita stimulated the specialised search for pollucite mineralisation in the frame of the exploration boom for Li and rare metals in pegmatites. In Western Australia, the Meso- to Neo-Archean units in the Yilgarn and Pilbara cratons are known to host many LCT pegmatites, among them world-class economic deposits as Greenbushes (Li-Ta-Sn) and Wodgina (Li-Ta-Sn). Geological mapping programmes by the Geological Survey of Western Australia and the National Geological Survey of Australia, as well as countless prospecting and exploration attempts, could identify a large number of LCT pegmatites. Due to this potential, the Rockwood Lithium GmbH at Frankfurt/Main (Germany) initiates and funds the exploration on LCT pegmatites with a special focus on Cs. The first author participated as investigator in such campaigns between July 2011 and June 2016, where a total of 19 pegmatite districts were inspected and sampled. The second author acted as the principal supervisor of the project. As the search for massive Cs-pollucite mineralisation is influenced by genetic concepts on their formation, the

Bikita pegmatite was included in the study. This book presents the analytical results and their interpretations, generated during the intensive search to find one more deposit of a yet merely unique mineralisation type on the planet Earth.

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Freiberg, Germany  
Crawley, Australia  
Frankfurt am Main, Germany  
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# Chapter 1

## Introduction to Archean Rare-Metal Pegmatites



### 1.1 The Alkali Metal Cesium

The element Cesium was first described by the German chemist Robert Wilhelm Bunsen and the physicist Gustav Robert Kirchhoff during the investigation of mineral water from Dürkheim (Kirchhoff and Bunsen 1861). Cesium was the first element that was discovered by emission spectroscopy and is characterised by a set of bright blue lines. Due to this, Kirchhoff and Bunsen (1861) named the newly discovered element *caesius*, the Latin word for “sky-blue”. Cesium is a chemical element belonging to the subgroup Ia of the alkali-metals in the periodic table. It is a silvery-gold, soft, extremely reactive and pyrophoric metal. Cs has physical and chemical properties similar to other alkali metals like Rb or K, with a large ionic radius of 1.65 Å, and belongs to the large ion lithophile elements (LILE). It has rather low melting (28.7 °C) and boiling points (668 °C), like Hg (Bick et al. 2010). Cesium predominantly forms compounds with halogens (CsF, CsCl) and oxygen as Cs<sub>2</sub>O (Wedepohl 1978). Natural Cs compounds as CsCl are only faintly toxic, and are not considered as a significant environmental hazard (Pinsky et al. 1981). As Cs exhibits an extremely low ionisation potential, it is far more reactive than Li, Na or K and still pronouncedly more reactive than Rb. When exposed to air, an explosion-like oxidation reaction will form cesium superoxide CsO<sub>2</sub>. In contact with water, Cs reacts vigorously and forms cesium hydroxide and hydrogen gas, with the latter igniting spontaneously (Bick et al. 2010). Although Cs has a total of 39 known isotopes, with mass numbers ranging from 112 to 155, only the <sup>133</sup>Cs is natural (Audi et al. 2003).

The cesium market is very small. As a result, data on Cs resources and production are not available or very limited. According to USGS-Cs-2017 the main pollucite zone at Tanco LCT pegmatite deposit in Canada comprises ~120,000 tons of Cs<sub>2</sub>O contained in pollucite ore, at ore grades of ~23.3 wt% Cs<sub>2</sub>O. Additional reserves are reported from Zimbabwe (~60,000 t) and Namibia (30,000 t). The annual world

consumption in 1978 was about 20 t of Cs, as metal and in compounds, and increased during the last decades. However, the market for Cs metal is still in the lower tens of thousands kilograms range per annum.

The first comprehensive studies on the distribution and behaviour of Cs on the Earth concerned its distribution in minerals and rocks (Horstman 1957; Wedepohl 1978; Barnes et al. 2012), or its interactions in host rocks of natural hydrothermal systems (Ellis and Mahon 1977; Keith et al. 1983). More recent studies concerned the behaviour of Cs during metamorphism and melting in subduction zone settings (Hart and Reid 1991; Hall et al. 1993; Bebout et al. 2007; Xiao et al. 2012), or in dependency of the water content of granitic melts (Watson 1979). The behaviour of Cs during the magmatic to hydrothermal processes, and the concepts of LCT pegmatite formation were later picked up and expanded in numerous studies by several working groups (Černý et al. 1985; Icenhower and London 1995; London 2008; Thomas and Davidson 2012).

According to McDonough et al. (1992), about 55% of Cs on Earth occurs in the continental crust, 4% of the Cs is incorporated in the residual mantle, and the remaining 40% of the element remain in the less depleted mantle reservoir. The concentration of Cs in the primitive mantle was estimated by Lyubetskaya and Korenaga (2007) to be 16 ppb. The average concentration of Cs in the upper crust has been estimated to be 4–5 ppm (Taylor and McLennan 1985; Rudnick and Gao 2014), while the lower crust has a Cs abundance of 0.5 ppm Cs (McDonough et al. 1992). Based on a bulk composition derived from 70% lower crust and 30% upper crust, an average content of about 2.1 ppm Cs can be estimated for the total continental crust, and compared to estimated 0.023 ppm Cs for the silicate earth. Ultramafic rocks contain <1 ppm Cs, however, some Archean mantle eclogites and peridotites have remarkably higher Cs of up to 9 ppm (McDonough et al. 1992). The average abundance in igneous rocks ranges from <1 ppm in mafites to about 10 ppm Cs in granitoids (Hall et al. 1993). Some highly fractionated evolved Permo-Carboniferous granites and lamprophyres of the Erzgebirge (Germany) can contain up to 204 ppm and 104 ppm Cs, respectively (Seifert 2008). Lower Permian Sn-F-enriched rhyolitic ignimbrites of the Sub-Erzgebirge basin show Cs contents up to 174 ppm (Seifert 2008). In Zinnwaldite from the Li-Sn greisen deposit Zinnwald (Germany) Cs contents of up to 750 ppm were measured (Neßler et al. 2017). The high-F topaz rhyolite from the Tertiary Spor Mountain Formation (Utah, USA) shows a Cs enrichment of up to 87 ppm (Dailey et al. 2018). Sedimentary rocks have an average between 4 and 12 ppm Cs, and clay minerals like kaolinite, bentonite, illite show a modest enrichment up to 17 ppm Cs (Horstman 1957). Oceanic water contains only 0.37 ppb Cs, but in potassic salt an average of 56 ppm Cs can be found (Osichkina 2006).

## 1.2 Mineralogy and Geochemistry of Cesium

As the Cs shares many properties with other alkali metals as Na, K or Rb, it occurs as trace element in feldspar or mica. Certain geological processes are capable to enrich