



Primary and secondary niobium mineral deposits associated with carbonatites



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ABSTRACT

This work reviews the character and origin of primary and supergene economic deposits of niobium associated with carbonatites. The Brazilian supergene deposits account for about 92% of the total worldwide production of Nb, with the primary St. Honoré carbonatite and other sources accounting for only for 7 and 1%, respectively. The emphasis of the review is upon the styles of Nb mineralization and the geological factors which lead to economic concentrations of Nb-bearing minerals. Primary economic deposits of Nb are associated principally with carbonatites found in diverse types of plutonic alkaline rock complexes. Primary magmas are principally those of the melilitite, nephelinite and aillikite clans. Although many primary niobium deposits are associated with carbonatites, ijolites and syenites in the same alkaline complexes can also contain significant Nb mineralization in the form of niobian titanite and diverse Nb–Zr-silicates (marianoite-wöhlerite); these potential sources of Nb have not as yet been explored or exploited. Primary Nb deposits can be regarded as large tonnage, low grade (typically <1 wt.% Nb₂O₅) disseminated ore deposits. Niobium is hosted principally by diverse Na–Ca–U-pyrochlores, ferrocolumbite and fersmite. Every actual, and potential, primary Nb deposit is unique with respect to the varieties of pyrochlore present; extent of replacement by other minerals; and degree of alteration by deuteric/hydrothermal fluids. Within a given occurrence individual petrographically-defined units of carbonatite contain distinct suites of pyrochlore. Bulk rock analysis for Nb gives no indication of the style of mineralization and provides no information of use regarding beneficiation of the ore. Evaluation of any Nb deposit requires extensive definition drilling and detailed mineralogical studies. Primary Nb deposits result from the early crystallization of Nb-bearing minerals in magma chambers followed by crystal fractionation, magma mixing, and redistribution of Nb-minerals by density currents. Supergene Nb deposits occur in laterites formed by extensive weathering of primary carbonatites. The process results in the decomposition of apatite and magnetite, removal of soluble carbonates and physical concentration of resistant primary pyrochlore. Intense lateritization results initially in the replacement of primary pyrochlores by supergene, commonly Ba, Sr, K or Pb-bearing pyrochlores, and ultimately complete decomposition of pyrochlore and formation of Nb-bearing rutile, brookite, and anatase. The Nb contents of the laterites can be enriched up to 10 times or more above those of the primary carbonatite. Commonly, pyrochlores in laterites are fine grained and intimately intergrown with hematite, goethite and minerals of the crandallite group. The different styles of mineralization of primary and secondary Nb deposits require different methods of ore beneficiation.

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1. Introduction

Niobium (Nb) is a strategic metal with a wide variety of uses ranging from niobium carbide- and niobium nitride-steel alloys through piezoelectric compounds, such as LiNbO₃, to superconducting niobium–tin magnets. Currently, there are only three operating Nb-mines [Araxá and Catalão-II (Brazil) and St. Honoré (Canada)]. All produce ferroniobium alloy from pyrochlore, with the Brazilian supergene deposits accounting for about 92% of the total worldwide production.

St. Honoré and other sources account for only for 7 and 1%, respectively. Mining at the Catalão-I carbonatite was discontinued in 2001, although there is a significant residual reserve of 19 Mt with a grade of 1.1.9 wt.% Nb₂O₅ (Cordeiro et al., 2011). Many other occurrences of carbonatite are currently being evaluated [e.g. Aley and Upper Fir (Canada); Elk Creek (USA)] or re-evaluated [e.g. Oka (Canada); Fen (Norway); Panda Hill (Tanzania)] for their economic potential. Although most actual and potential Nb deposits contain pyrochlores with tantalum (Ta) in solid solution it does not follow that a particular Nb occurrence is also an economic source of Ta (and *vice versa*), as the style of mineralization of Nb and Ta deposits is very different (see below).

This paper does not attempt to list, or describe, *all* potential Nb deposits and their estimated tonnage and grade. Such lists can be found

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in the summaries by [Cordeiro et al. \(2011\)](#), [Berger et al. \(2009\)](#), [Pell \(1994, 1996\)](#), or [Richardson and Birkett \(1996\)](#), with the caveat that these lists are not comprehensive with respect to many Angolan, Indian, Chinese, and Russia occurrences of carbonatites and alkaline rocks. *This work is concerned primarily with the mineralogy, petrology, and genesis of Nb deposits associated with carbonatites and the factors which are significant in determining the economic potential of an occurrence.*

In general, primary Nb mineral deposits are associated with two groups of igneous rocks: (1) carbonatites and associated undersaturated silicate rocks such as the ijolite suite; and (2) over-saturated alkaline-to-peralkaline granitoids and syenites. However, note that “carbonatites *sensu lato*” can be found in association with either group (see below), and some carbonatites have no discernible relationships to any silicate rocks ([Mitchell, 2005a](#)). Secondary, or supergene, Nb mineral deposits form in zones of lateritic weathering above primary deposits. The process leads to significant enrichment in Nb, typically by a factor of 10 or more, above the grade of the primary sources. The Brazilian deposits at Araxá, Catalão-I and II, and Seis Lagos are examples of extreme secondary enrichment. Similar supergene occurrences occur at Lueshe and Bingo (D.R. Congo), Mabounié (Gabon), Sukulu (Uganda), and Mt. Weld (Australia).

The association of significant Nb mineralization with at least two groups of rocks which have very different petrogenesis implies that there cannot be a single model for the genesis of all Nb deposits. Currently, most carbonatites are considered to be derived by fractional crystallization or liquid immiscibility from melilititic or nephelinitic mantle-derived magmas ([Mitchell, 2005a](#)), whereas peralkaline A-type granitic magmas might be formed by partial melting of metasomatized lower crust ([Martin, 2006, 2012](#)). The genesis of both magma types remains controversial and discussion of their diverse genetic hypotheses is well beyond the scope of this review.

To date, all *major* operating and former (Oka, Fen, Lueshe) Nb mines have been developed in primary carbonatites associated with undersaturated silicate rock complexes, and consequently are the focus of this work. Currently, there is interest in the evaluation of several A-type syenite/granitoid complexes for their Nb potential. These include: Motzfeldt, Greenland ([McCreath et al., 2013; Tukainen, 1988](#)); Strange Lake, Canada ([Salvi and Williams-Jones, 2006](#)), Thor Lake, Canada ([Sheard et al., 2012](#)); Khaldaza-Buregtey and Khan-Bogda, Mongolia ([Kovalenko et al., 1995](#)); Ghurrayah, Saudi Arabia ([Küster, 2009](#)). None of these occurrences have, to this time, any proven economic potential for Nb alone, as Nb grades are low (0.1 to 1 wt.% Nb₂O₅), and the complexes are typically considered as multi-commodity Nb–Ta–Y–REE deposits rather than single sources of niobium. The only operating Nb mine in under-saturated peralkaline syenites is the Karnasurt mine ([Kremenetsky et al., 2009; Pekov, 2000](#)) in the Iujavrites of the Lovozero complex from which a concentrate with about 8 wt.% Nb₂O₅ is produced from loparite, a Nb–REE-bearing perovskite group mineral.

2. Aspects of niobium geochemistry

The formation of a potential Nb deposit requires concentration of the element to the point at which Nb minerals form during the crystallization of a parental magma. In unevolved silicate or carbonate magmas there are few liquidus minerals which can sequester Nb, due to the penchant for the element to form complex anions (NbO₄³⁻; NbO₆⁷⁻; Nb₂O₆²⁻) which cannot be accommodated at lattice sites in common minerals such as olivine, pyroxene, feldspar, and carbonates ([Parker and Fleischer, 1968](#)). Thus, the Nb content of silicate and/or carbonate melts tends to increase with differentiation until the solubility of Nb is reached with the formation of Nb minerals whose structure is based upon these complex ions. Typically, basaltic rocks contain less than 30 ppm Nb, whereas nephelinites and melilitites are relatively enriched in Nb and can contain up to 400 ppm Nb ([Ivanikov et al., 1998; Klaudius and Keller, 2006](#)). Concentration factors of 150–200 or 6–15 are thus required to reach the Nb contents of some typical primary

carbonatite-hosted Nb deposits (3000–5000 ppm Nb; see below). Nb deposits are not associated with common continental or mid-oceanic ridge basaltic magmatism. Currently, the petrogenesis of cratonic rift-related nephelinite–melilitite magmas is considered to be a complex multi-stage process involving partial melting of carbonated metasomatized asthenospheric mantle ([Dawson, 2008](#)); this mantle being enriched in volatiles, Nb, Zr, Ti, and rare earth elements (REEs). The ultimate source of the Nb is either intrinsic, and mantle-derived, and/or recycled subducted crustal material.

With respect to niobium–yttrium–fluorine-rich (NYF) peralkaline granite/syenite-hosted Nb deposits it is apparent that mineralogically simple lower or mid-crustal rocks with Nb contents of 5–10 ppm Nb ([Rudnick and Gao, 2003](#)) cannot serve as a source without further enrichment by metasomatic processes prior to their partial melting, as advocated for example by [Martin \(2012, 2006\)](#). Typical “barren” peralkaline granites contain up to 550 ppm Nb ([Mitchell et al., 1993; Stuckless et al., 1986](#)). The origins of the rare metal enrichment in such NYF-A-type peralkaline granites remains undetermined, but it is evident that fluorine must play a significant role in Nb concentration and transport given that Nb can form a variety of fluoride and oxyfluoride complexes, and fluoride minerals are common in NYF-pegmatites containing F-bearing pyrochlore. In common with carbonatite-hosted Nb deposits the ultimate source of the Nb could be in the lower mantle and/or recycled lower crust, but the major differences between magma types and styles of mineralization preclude any common genesis for the Nb mineralization.

Many F-rich lithium–cesium–tantalum (LCT) granites contain minerals that are significantly enriched in Nb. For example, the LCT cryolite–albite granite ([Bastos Neto et al., 2009](#)) at Pitinga (Brazil), although primarily a Sn deposit, produces Nb and Ta as by-products from niobian cassiterite. Although pyrochlore does occur in the mineral suite of LCT-granites, these differ notably from NYF-granites as the Nb is hosted primarily as solid solutions in Sn–Ti–Ta minerals such as cassiterite, ilmenite, rutile, ixiolite, wodginite, and columbite–tantalite group minerals. The LCT-granites, and columbite–tantalite placers (including the notorious “coltan”) derived from such granites, account for only about 1% of the world wide Nb production.

3. Mineralogy of Niobium

The mineralogy of Nb is complicated, and dominated by complex oxides and silicates many of which contain lattice vacancies, hydroxyl groups, fluorine and water. Currently, about 115 Nb-dominant or Nb-bearing oxides are recognized as mineral species by the International Mineralogical Association (IMA). Many of these belong to the pyrochlore supergroup, the common ore minerals of Nb deposits (see below), perovskite group minerals, or the wodginite and columbite–tantalite groups (typical of LCT-granites). There are about 80 IMA approved silicates containing essential Nb. Many of these are titanates belonging to the eudialyte group. In addition, Nb is a common substituting minor-to-major element in many titanates (rutile, ilmenite, titanite), zirconolite, and other titanates such as baotite, lamprophyllite, and chevkinite.

[Table 1](#) lists the common niobium oxide and silicates found in Nb mineral deposits. Of these, the oxides are by far the most important as they are the more amenable to ore beneficiation and conversion to metal. However, it is not generally realized that in some carbonatite–alkaline rock complexes the overall abundance of Nb in rocks containing Nb-silicates, such as marianoite–wöhlerite solid solutions, niocalite, niobian rutile or niobian titanite, might exceed that of associated pyrochlore-bearing carbonatites. To date there are no investigations into the Nb-potential of such silicate rocks or the beneficiation of these minerals.

[Table 1](#) also indicates the dominant Nb-bearing minerals in carbonatites *versus* those in NYF and LCT granites/syenites. This distinction should be taken only as a guide to the style of Nb mineralization with the proviso that modal amounts can vary widely. It is actually

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