



A global review on agpaitic rocks



Michael A.W. Marks*, Gregor Markl

Universität Tübingen, FB Geowissenschaften, Wilhelmstrasse 56, 72074 Tübingen, Germany

ARTICLE INFO

Keywords:

Peralkaline
Miaskitic
Agpaitic
Hyperagpaitic
Redox conditions
Magma differentiation

ABSTRACT

Peralkaline igneous rocks are defined by a molar $(\text{Na} + \text{K})/\text{Al}$ ratio > 1 and are subdivided into miaskitic and agpaitic varieties depending on their mineralogy. In the more common miaskitic types, rare earth elements (REEs) and high field strength elements (HFSEs) are largely stored in zircon and titanite, while agpaitic varieties contain a wealth of mostly halogen-bearing Na-Ca-HFSE minerals instead. Among those, minerals of the eudialyte, rinkite, and wöhlerite groups are the most common ones. The present review on the geological and mineralogical information available on agpaitic rocks provides a summary of the fluid inclusion record of miaskitic and agpaitic rocks as fluids play a key role in the evolution of peralkaline rocks.

Magmas that crystallize peralkaline rocks are generally believed to originate from low-degree partial melting of geochemically enriched mantle lithologies, combined with prolonged differentiation processes at shallow crustal levels. Agpaitic and hyperagpaitic rocks (the latter containing appreciable amounts of water-soluble minerals) represent the most evolved stages of peralkaline systems. They form either parts of plutonic to subvolcanic composite magmatic complexes, which consist of several agpaitic and/or miaskitic intrusive units, or they occur as sills, laccoliths, domes, dykes, or even as lavas. However, as agpaitic rocks are notably rare compared to miaskitic rocks (about 100 vs. several thousand occurrences worldwide), their formation requires special conditions that are not generally met during the evolution of peralkaline rocks. Despite their rarity, agpaitic and hyperagpaitic rocks form important deposits of critical metals such as REE, Zr, Nb, and U and are interesting targets for otherwise rare elements such as F, Be, Sn, Zn, and Ga.

The relative timing when magmas reach their agpaitic stage is highly variable. Magmatic–agpaitic assemblages can form only if early-magmatic crystallization conditions were reduced enough (low f_{O_2}) to enable subsequent Fe enrichment, an increase in peralkalinity, retention of halogens, and extreme enrichment of HFSEs in the evolving magmas, as only these contribute to the direct crystallization of agpaitic minerals. Late-magmatic interstitial agpaitic assemblages indicate that the required enrichment levels of the above-mentioned constituents were reached only during the final differentiation stages of magmas. Hydrothermal agpaitic assemblages precipitate from highly saline brines released from peralkaline magmas and are capable of transporting HFSEs. All three varieties of agpaitic assemblages occur in plutonic, subvolcanic, and volcanic rocks. Although many modern and detailed studies have dealt with plutonic–subvolcanic agpaitic rocks, most volcanic occurrences are insufficiently studied, mainly because of difficult outcrop or logistic situations. However, especially the volcanic examples raise questions on the details of why and how degassing of halogens at such shallow emplacement levels is sufficiently prevented to precipitate halogen-bearing agpaitic assemblages. Thus, a thorough geochemical and petrological investigation of such localities is desired.

The presently valid definitions of agpaitic and miaskitic rocks are not appropriate, and therefore, alternative definitions are suggested. Similarly, the frequently used classification scheme for nepheline syenites must be abandoned as it is inconsistent and excludes very similar mineral assemblages observed in other partly even quartz-bearing rock types. Variable processes may produce sequences of mineral assemblages that belong to different groups of this classification. Therefore, we suggest that rather than dividing agpaitic rocks into specific subgroups, careful textural studies that distinguish early-magmatic, late-magmatic, and hydrothermal phase assemblages are warranted. This is the only way to understand the effect of various physicochemical parameters (such as P , T , f_{O_2} , a_{SiO_2} , $a_{\text{H}_2\text{O}}$, peralkalinity, and the activity of other compounds including halogens) during different evolutionary stages of these mineralogically and texturally diverse rocks.

* Corresponding author.

E-mail address: michael.marks@uni-tuebingen.de (M.A.W. Marks).

1. Introduction

Peralkaline igneous rocks are defined by a molar $(\text{Na} + \text{K})/\text{Al}$ ratio > 1 and include intrusive and extrusive silica-oversaturated (granitic/rhyolitic), silica-saturated (syenitic/trachytic), and silica-undersaturated (nepheline syenitic to foidolitic/phonolitic to foiditic) rocks (e.g., Le Maitre, 2003; Frost and Frost, 2008, 2010). Most peralkaline rocks are rich in large ion lithophile elements (LILE, such as Li, Na, K, Rb, and Cs), halogens (F, Cl, Br, and I), rare earth elements (REEs), high field strength elements (HFSEs, such as Zr, Hf, Nb, Ta, and U), and otherwise relatively rare elements such as Be, Sn, Zn, and Ga (e.g., Kogarko, 1980; Sørensen, 1992; Bailey et al., 2001).

In some cases, the extreme enrichment of alkalis, halogens, HFSEs, and REEs during the differentiation of peralkaline magmas may result in the precipitation of a wealth of otherwise rare minerals including F-minerals (villiamite), Cl-minerals (sodalite), and various typical halogen-bearing Na-Ca-HFSE minerals (Table 1), the most common of them being eudialyte-group minerals (EGMs; e.g., Sørensen, 1997; Johnsen et al., 2003; Rastsvetaeva, 2007; Pfaff et al., 2010) and members of the rinkite and wöhlerite groups (e.g., Merlino and Perchiazzi, 1988; Chakhmouradian et al., 2008; Sokolova and Cámara, 2017). The presence of these diverse and structurally complex HFSEs defines the so-called agpaitic rocks as opposed to miaskitic rocks, in which HFSEs are largely hosted by zircon and titanite (Khomyakov, 1995; Sørensen, 1997; Le Maitre, 2003; Andersen et al., 2010; Marks et al., 2011), as is typical of most other igneous rocks.

The extreme geochemical composition of agpaitic rocks results in a unique wealth of different minerals. Many occurrences of agpaitic rocks are type localities for several minerals, with the extreme examples of Khibina (Russia, $N = 120$), Lovozero (Russia, $N = 106$), Mont Saint-Hilaire (Canada, $N = 65$), Dara-i-Pioz (Tajikistan, $N = 35$), and Ilímaussaq (Greenland, $N = 33$), summing up to > 350 types of minerals (mindat.org). As many agpaitic minerals contain halogens and as other halogen-bearing minerals such as sodalite and fluorite are typically associated, the retention and release of fluids carrying alkalis, halogens (F and Cl), and other fluid-mobile components during the evolution of peralkaline magmas are of critical importance for their formation (e.g., Markl et al., 2001; Andersen et al., 2010).

The magmas eventually forming agpaitic rocks are mantle derived. A combination of low melting degrees of a geochemically pre-enriched magma source and subsequent differentiation at low oxygen fugacity (f_{O_2}) and water activity ($a_{\text{H}_2\text{O}}$) is probably responsible for the unusual geochemical composition of agpaitic rocks (e.g., Kogarko, 1974; Harris, 1983; Larsen and Sørensen, 1987; Caroff et al., 1993; Kramm and Kogarko, 1994; Sørensen, 1997; Frisch and Abdel-Rahman, 1999; Markl et al., 2010). Although agpaitic rocks are relatively rare and often considered mineralogically exotic, they are of large economic interest as they represent some of the most promising sources for future HFSE and REE supply (e.g., Smith et al., 2016; Goodenough et al., 2016).

Reviews on agpaitic rocks have been presented by Sørensen (1960, 1974, 1997) and Khomyakov (1995). Since then, many detailed textural, mineralogical, petrological, and geochemical works on agpaitic and very similar rock types have been published, which revealed the complex evolution of such rocks. Therefore, we consider it timely to present an overview on the present knowledge on these diverse rocks to provide directions for future research.

The most common and classical cases of agpaitic rocks are those

containing EGM-bearing assemblages. We review the information available for the 105 EGM-bearing localities known to date (Fig. 1; Table 2) and compare them with those of other igneous rocks containing similar HFSE-rich mineral assemblages. We provide an overview on the fluid inclusion data presently available for miaskitic and agpaitic rocks and propose models for the formation of orthomagmatic, late-magmatic, and hydrothermal agpaitic mineral assemblages.

Khomyakov (1995) suggested a classification system for nepheline syenites on the basis of the presence of mostly accessory silicate minerals of the general formula $\text{A}_x\text{M}_y\text{Si}_p\text{O}_q$ ($A = \text{Na}, \text{K}$, and other strong bases; $M = \text{Nb}, \text{Ti}, \text{Zr}, \text{Be}$, and other Al-substituting elements). The compositional parameters x , y , and p were used for calculating the so-called alkalinity modulus ($K_{\text{alk}} = (x * 100) / (x + y + p)$) to distinguish five subgroups, namely miaskitic ($K_{\text{alk}} \ll 15\%$), low agpaitic ($K_{\text{alk}} = 15\text{--}25\%$), medium agpaitic ($K_{\text{alk}} = 25\text{--}35\%$), highly agpaitic ($K_{\text{alk}} = 35\text{--}40\%$), and hyperagpaitic ($K_{\text{alk}} > 40\%$) rocks, each of them defined by typical mineral assemblages (Table 3). Although helpful at a first glance, we consider this scheme to be insufficient and not appropriate because (i) early-magmatic, late-magmatic, and hydrothermal agpaitic assemblages were not distinguished, (ii) the often complex textural relations between the various mineral assemblages were not considered, (iii) quartz-bearing syenites and peralkaline granites were excluded from this scheme, and (iv) very similar mineral assemblages in some nepheline syenites and in potassic-ultrapotassic rocks were not considered. This situation is unsatisfactory and causes considerable confusion in the literature regarding whether a given rock should be called agpaitic or not and how to name alkaline rocks properly. Therefore, we propose redefinitions for the terms agpaitic and miaskitic and suggest a descriptive characterization of agpaitic rocks according to textural and mineralogical criteria.

2. Geology of agpaitic rocks

We compiled 105 EGM-bearing localities of agpaitic rocks described in the literature (Table 2) along with their age, field expression, EGM textures, rock associations, and several key references for each locality. The level of detail concerning the geological, mineralogical, and petrological information among the listed localities varies considerably. The classical localities (e.g., Ilímaussaq, Khibina, Lovozero, Mont Saint-Hilaire, and Tamazeght) have been intensely studied since the 19th century. Much of our modern views concerning the origin and evolution of agpaitic rocks originate from the study of these relatively few occurrences. Detailed work on some less studied localities became available in the last decades (e.g., Langesundfjord, Pilanesberg, Madagascar, Norra Kärr, Red Wine, and Kipawa). Many other occurrences, however, are only shortly mentioned in the accessible literature and clearly deserve further investigation (e.g., some of the occurrences in Brazil, Tajikistan, Kazakhstan, Alaska, and Libya). Some localities were only recently discovered (e.g., Sushina), partly in otherwise well-known alkaline provinces (e.g., Kaiserstuhl and Kovdor). Therefore, the presented list of EGM occurrences (Table 2) is probably not yet complete, and more localities may be added in the future.

2.1. Geodynamic setting and age distribution

The geodynamic settings in which agpaitic rocks occur resemble those for peralkaline rocks in general (e.g., Sørensen, 1974; Fitton and Upton, 1987 and references therein), including (i) continental rifts (e.g.,

Download English Version:

<https://daneshyari.com/en/article/5785059>

Download Persian Version:

<https://daneshyari.com/article/5785059>

[Daneshyari.com](https://daneshyari.com)