

LETTER

Native aluminum: Does it exist?

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ABSTRACT

Several papers reporting exotic native elements have been published within the last few decades. The “native” occurrences described are rather dubious in view of the lack of solid proof of their relationships with the host-rock minerals. Consequently, the genetic models proposed ranging from bio-reduction to the influence of deep-mantle, strongly reduced fluids, are somewhat speculative. Here we present data for a unique Al<sup>0</sup> flake protruding from the phlogopite matrix of a rock specimen collected from a desilicated pegmatite vein. The geologic setting suggests two processes that might have played a key role in the Al<sup>0</sup> formation: (1) desilication of pegmatite, resulting in its Al residual enrichment; and (2) serpentinization of an ultramafic body, providing a strongly reduced front (H<sub>2</sub> and hydrocarbons) toward the serpentinite/pegmatite contact. These processes have presumably led to the reduction of Al to Al<sup>0</sup> at discrete sites of alumina-rich minerals.

**Keywords:** Native Al, serpentinization, desilication, reduction, pegmatite

INTRODUCTION

The theoretical possibility of the natural existence of elements with a high affinity for O in a zero-valence state at crustal conditions has provoked the interest and imagination of scientists for many years, and reports on the occurrence of unusual native elements have always aroused surprise. The discoveries of Al<sup>0</sup> (Okrugin et al. 1981), Si<sup>0</sup> (Robinson et al. 2004), and Ti<sup>0</sup> (Distler et al. 2004), all claimed to be native, are still a matter of ongoing debate. The first description of Al<sup>0</sup> flakes found in crushed rock samples claimed that these were native Al occurrences (Oleinikov et al. 1978). A response (Sobolev 1979) to this report subjected it to criticism, and warned that sample contamination could lead to misinformation. Nonetheless, these first investigators of Al<sup>0</sup> flakes submitted a proposal (numbered IMA 1980-085) for a new mineral, native Al, to the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA). The relevant annual CNMMN report on new minerals (Fleischer et al. 1980) gave brief information on the Al<sup>0</sup> occurrence described by Oleinikov et al. (1978), indicated that this mineral had not been approved, and added an accompanying note by the senior author: “This seems extremely improbable from thermodynamic considerations.” Later, the CNMMN voting was suspended twice and the proposers were urged to provide more information, which they did in two consecutive proposals (IMA 1980-085a and IMA 1980-085a'). On the basis of the last revised proposal, the mineral and the name aluminum were both approved, and the results were announced in 1983 (CNMMN Chairman J. Mandarino's memorandum). However, a review of all three proposals shows that: (1) none of them presents a photograph of Al<sup>0</sup> intergrown with aluminosilicates/silicates;

and (2) they all describe Al<sup>0</sup> flakes obtained from crushed rock. These deficiencies make the native Al proposals unconvincing, and well-known textbooks on mineralogy, such as Hey's Mineral Index (Clark 1993), comment on this mineral: “Mineral species of questionable validity.”

The validation of native Al apparently prompted an avalanche of reports on unusual native metals and alloys in various rock types (Novgorodova 1994 and references therein). These spawned controversies and raised questions that are still awaiting answers. Do the elements with a high affinity for O exist in zero-valence states in an oxic planet like Earth? The principal deficiencies that create doubts of possible anthropogenic contamination in the majority of the works are: (1) a substantial proportion of the reports of “native” metals is based on occurrences in placers, sediments, soils and crushed rock samples; and (2) unconvincing documentation of “undoubted” intergrowths of native metals with silicates, without any unequivocal photos of these native metal/silicate relations. To our knowledge there is only one unambiguous report of a native Al occurrence (Korzinsky et al. 1995), although it describes man-mediated natural Al<sup>0</sup> precipitation in recent fumaroles at the Kudriavyy Volcano, Kuril Arc.

Here we report on an exceptional metallic Al flake protruding from a rock specimen with phlogopite and emerald in a pegmatite vein in the Rila Mountain (Bulgaria). This contribution addresses the composition and origin of native Al.

GEOLOGIC SETTING

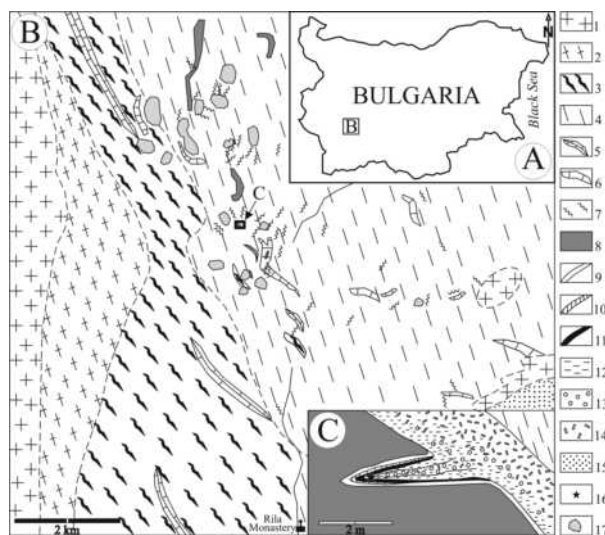
Northwest Rila Mountain (Fig. 1a) is composed of intrusive (granite) and metamorphic (gneiss, amphibolite, serpentinite) rocks (Fig. 1b). The metamorphic units are cut by a variety of pegmatite veins and marble lenses. The host for the native Al is a gem pegmatite vein (~20 × 3 m) that has been intruded between a

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small serpentized ultrabasic body and biotite gneiss, and which contains plagioclase, phlogopite, Cr-bearing muscovite, apatite, Be-bearing margarite, beryl, chrysoberyl, emerald, native Bi, Nb-Ta oxides, and garnet (Fig. 1c; Arnaudov 1975). The pegmatite is asymmetrically desilicated—substantially along the contact with the serpentized ultrabasic unit, and slightly (with plagioclase, mica, and quartz) at the contact with the gneiss (Petrušsenko et al. 1966). A small, completely desilicated apophysis of the pegmatite vein is intruded into the serpentized ultrabasic body and has a zonal texture (Fig. 1c; Petrušsenko et al. 1966).

## MATERIAL AND METHODS

During a field trip to the NW Rila Mountain in the early 1960s, one of us (V.A.) investigated the desilicated pegmatite apophysis and, from the phlogopite zone (Fig. 1c), collected a rock specimen with a protruding metallic flake visible to the naked eye (Fig. 2). After a preliminary description (Arnaudov 2006), we studied this metallic flake with X-ray diffraction (XRD) performed directly on the natural specimen (Rigaku D-MAX RAPID X-ray diffractometer, CuK $\alpha$  radiation, curved graphite crystal monochromator, Imaging Plate Detector, 0.1 mm collimator, measuring range 6–90 °2 $\theta$ , 40 kV, 30 mA, 4 h exposure time). Scanning electron microscope (SEM) observations were made on the uncoated rock specimen using a JEOL JSM-5410LV electron microscope with EDX detector. A particle-induced X-ray emission [PIXE; Si(Li) detector of 80 mm<sup>2</sup>, 150  $\mu$ m Be windows, and 6 mm air layer] and Rutherford backscattering spectroscopy (RBS; annular particle detector, solid angle 18 msr) (using 3 MeV H<sup>+</sup> and 2 MeV He<sup>2+</sup> ion beams) were used to obtain the composition (all elements heavier than Mg) and depth profiles, respectively, of the main elements of the metallic flake. Point measurements of interesting areas were made with the focused ion beam (20  $\times$  30  $\mu$ m). The areas were selected from an optical microscope (Olympus C3030-ADL) view or from elemental maps obtained with PIXE. The PIXE and RBS measurements were analyzed separately using the programs GupixWin (Campbell et al. 2000) and NDF (Barradas et al. 1997), respectively. Nuclear reaction analysis (NRA) (<sup>15</sup>N method; beam spot  $\leq$  1 mm<sup>2</sup>) was used to obtain a depth profile of H for the metallic flake.



**FIGURE 1.** (a) Inset: map of Bulgaria with the location of the study area in the Rila Mountain (b); (b) schematic geological map of the NW Rila Mountain (after Petrušsenko et al. 1966); (c) sketch map (not to scale at b) of the gem pegmatite (modified from Petrušsenko et al. 1966) with the location of the Al<sup>0</sup> occurrence. 1 = granite; 2 = amphibole-biotite gneiss; 3 = amphibolite; 4 = biotite gneiss; 5 = marble lenses; 6 = skarn zones; 7 = normal pegmatites; 8 = serpentized ultrabasic rocks; 9 = chlorite zone; 10 = tremolite zone; 11 = amphibole-phlogopite zone; 12 = phlogopite zone; 13 = beryl and emerald occurrences; 14 = plagioclase zone; 15 = alluvial deposits; 16 = Al<sup>0</sup> occurrence; 17 = lakes.

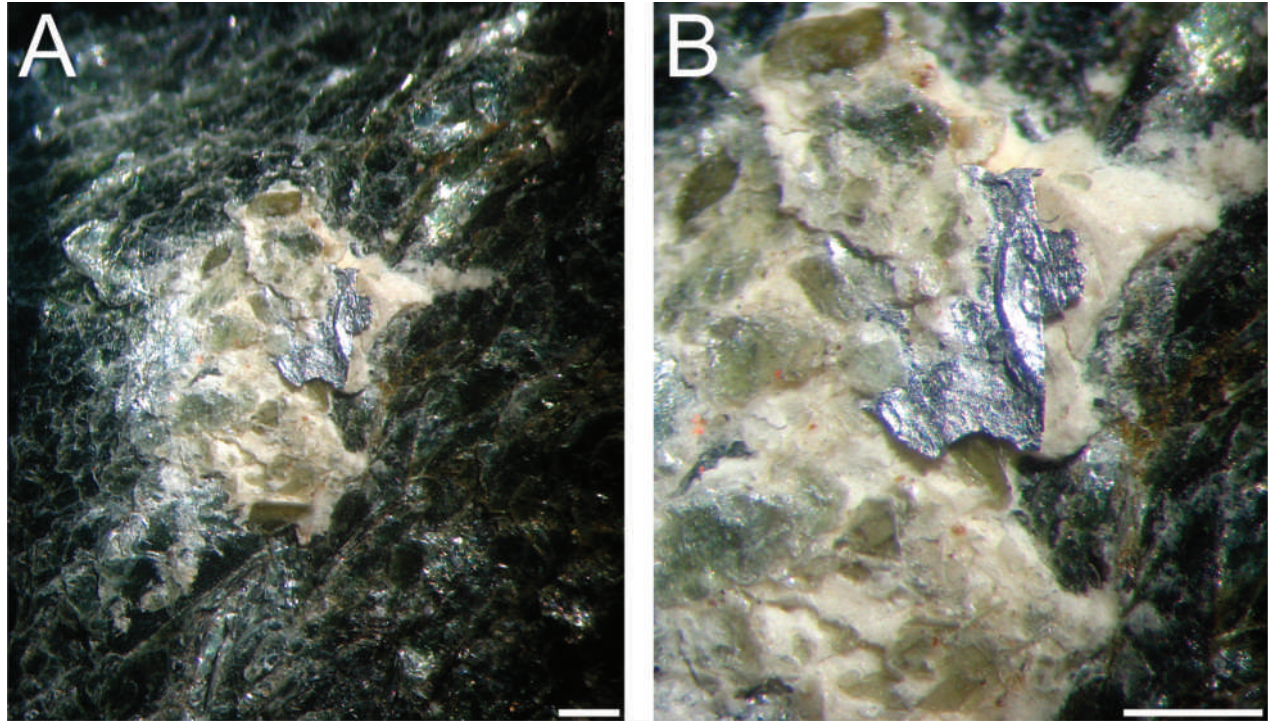
## RESULTS

The metallic flake is quite large (~2  $\times$  2 mm area, ~0.5 mm thickness), and occurs in a phlogopite matrix (Fig. 2) along with chrysoberyl, emerald, and apatite. It is silver-white, with a strong metallic luster. The XRD pattern of the metallic flake confirmed that it is Al<sup>0</sup> (Fig. 3). EDX data showed it is almost pure Al with minor Si and traces of Fe, Ca, and K. The PIXE study (Table 1) revealed that the Al<sup>0</sup> flake is inhomogeneous from point to point, and consists of ~90% Al. In addition to the elements analyzed by EDX, the Al<sup>0</sup> flake has traces of P, S, Cl, and Ti. The RBS depth profiling found that the Al<sup>0</sup> flake is coated by a thin (~100 nm) film with a double-layered structure (Fig. 4): the surface layer (~50 nm thick) contains C and O in addition to the Al, whereas the lower layer (~50 nm thick) shows only Al and O. NRA measurements failed to obtain the depth profile of H due to the uneven surface of the flake.

## DISCUSSION AND CONCLUDING REMARKS

The observation that the Al<sup>0</sup> flake protrudes from the phlogopite matrix (Fig. 2) suggests that it is a natural occurrence, and formed in situ. Additional evidence supporting the natural origin of the Al<sup>0</sup> flake is its composition (Table 1), which differs from that of anthropogenic aluminum alloys (Budinski and Budinski 1999). The main alloying elements (Cu and Mn) typical of industrial aluminum alloys are absent in the Al<sup>0</sup> flake. The origin of this native Al occurrence is enigmatic. Korzhinsky et al. (1995) found Al<sup>0</sup> particles in Cl-rich precipitates from fumaroles emitted at the Kudriavyy Volcano (Kuril Volcanic Arc) and argued that Al<sup>0</sup> is a result of the disproportionation of aluminum halides. Although the Al<sup>0</sup> flake we have studied contains ~0.4% Cl (Table 1), we do not regard this as unambiguous proof that the Al<sup>0</sup> was precipitated by the disproportionation of Al chlorides. The thin film containing C and O that envelopes the native Al flake (Fig. 4) implies that C-containing species may have participated in the Al<sup>0</sup> formation.

The geologic setting suggests two processes that may have played a key role in the formation of native Al in this case: (1) desilication of the pegmatite vein, and (2) serpentization of the ultrabasic body. The emplacement of the non-metamorphosed pegmatite vein along the contact between the serpentized ultrabasic rocks and biotite gneiss, and the pegmatite apophysis cross-cutting the ultrabasic rocks, suggests that the pegmatite is younger than the country rocks. Obviously there has been a small-scale contact-metasomatic event between two chemically different rocks—a silica-deficient rock (serpentized ultrabasic body) and a silica- and alumina-rich rock (pegmatite). During such an event, the silico-aluminous unit undergoes desilication, with Si being “pumped out” by the silicodeficient unit while Al, which is less mobile, remains in the protolith and recrystallizes as Al-rich minerals (e.g., Mercier et al. 1999). Quartz tends to disappear from the pegmatite, and concomitant silication of the host ultrabasic causes the development of phlogopite-rich borders along the pegmatite walls. This type of mineralization is bi-dimensional (planar), of relatively small size (meter-scale thickness and tens of meters in lateral extension) and with sharp mineral zonation with contacts parallel to the plane of mineralization. This is exactly what we observe (Fig. 1c). Desilication



**FIGURE 2.** (a) Photograph of the specimen with deep-green phlogopite and Al<sup>0</sup> flake (at the center); (b) close-up of the Al<sup>0</sup> flake shown at a. The Al<sup>0</sup> flake protrudes from the phlogopite matrix. Scale bar = 1 mm. The specimen (no. M.008465) is kept in the Laboratory for Geocollections at the Geological Institute of Bulgarian Academy of Sciences.

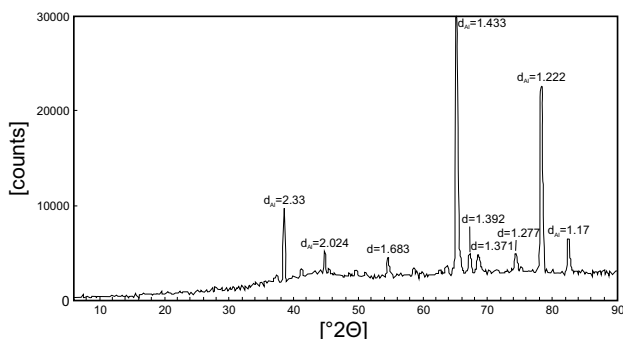
is the process that provides a relative Al excess in the pegmatite side of the contact with the ultrabasic body and in the pegmatite apophysis (formation of chrysoberyl, Be-bearing margarite, and Cr-bearing muscovite).

The hydration of olivine and orthopyroxene, accompanied by the conversion of Fe<sup>2+</sup> in silicates to Fe<sup>3+</sup> in magnetite during serpentinization, leads to the production of H<sub>2</sub>, and the conversion of dissolved CO<sub>2</sub> to reduced-C species, including CH<sub>4</sub>, in mafic/ultramafic rocks through Fischer-Tropsch type reactions (Berndt et al. 1996; Sleep et al. 2004). The production of hydrocarbon species is a common process in mafic/ultramafic rocks in the lower crust/upper mantle where water-based fluids interact with mafic mineral phases (Berndt et al. 1996; Kelley and Früh-

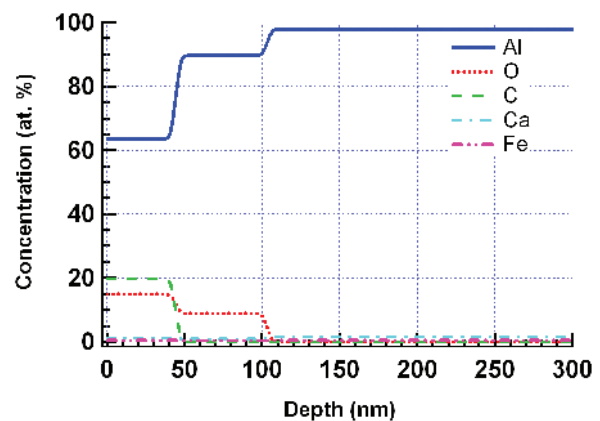
**TABLE 1.** Composition of Al<sup>0</sup> flake (PIXE data\*)

Point analysis no.	1-1	2-1	2-2
Al, wt%	87.5	88.8	94.9
Si	7.51	4.47	0.19
K	1.82	1.14	0.35
Ca	1.04	1.14	0.51
Fe	1.55	1.26	0.59
P	0.17	1.47	2.38
S	0.17	0.71	0.86
Cl	0.20	0.87	0.22
Ti, ppm	347	1070	293
Total, wt%	99.99	99.97	100.03

\* Average concentrations for point measurements under the assumption that the sample is homogeneous in depth and the only additional elements in the surface layers are C and O (see the RBS data). It should be noted that the sample is inhomogeneous and therefore these results may contain systematic deviations.



**FIGURE 3.** XRD pattern of the metallic flake ( $d$  spacings in angstroms). Unscribed  $d$  spacings belong to the whitish mineral surrounding the metallic flake. The relative intensities of the Al<sup>0</sup> peaks do not correspond to the Al<sup>0</sup> reference data due to the preferential orientation of the metallic flake.



**FIGURE 4.** RBS depth profile of the elements detected in the Al<sup>0</sup> flake.

Green 1999). The redox conditions of serpentinization approach those needed to stabilize native metals (Frost 1985; Berndt et al. 1996). We presume that, at the extremely reducing conditions of serpentinization, the reduced species ( $H_2$ ,  $CH_4$ ) migrating from the serpentinized ultramafic body through the desilicated pegmatite, reduced aluminum to  $Al^0$  at discrete points where there were Al-rich minerals. The oxide skin that envelopes the  $Al^0$  flake (Fig. 4) has protected it from later alteration.

We would not assert that phlogopite embedding the  $Al^0$  flake has been precursor of native Al in view of its low Al content [chemical formula  $KMg_3(Si_3Al)O_{10}(F,OH)_2$ , Al = 6.44 wt%; Kostov 1968]. The phlogopite has merely been the host for another Al-rich precursor. We may speculate that a possible candidate for an Al-rich precursor phase of the native Al may have been chrysoberyl (chemical formula  $BeAl_2O_4$ , Al = 42.5 wt%; Kostov 1968) observed as single crystals scattered in the phlogopite matrix (Arnaudov 1975).

As the serpentinization of mafic/ultramafic rocks of the lower crust/upper mantle is a widespread process on a global scale (Kelley and Früh-Green 1999), it represents an immense source of highly reduced gases. The extremely reduced front may provide the environment for the reduction of many elements to their zero-valence states. Since the reduction occurs at discrete sites on a micro-scale, the reduced mineral phases may later have been either re-oxidized or, if preserved, overlooked during investigation. Consequently, the extent of native metal formation under crustal conditions appears to be underestimated. Apparently serpentinization processes play a significant role in the cycles of certain elements, and the scale of this process has still not been properly evaluated.

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