Native Al and Si formation

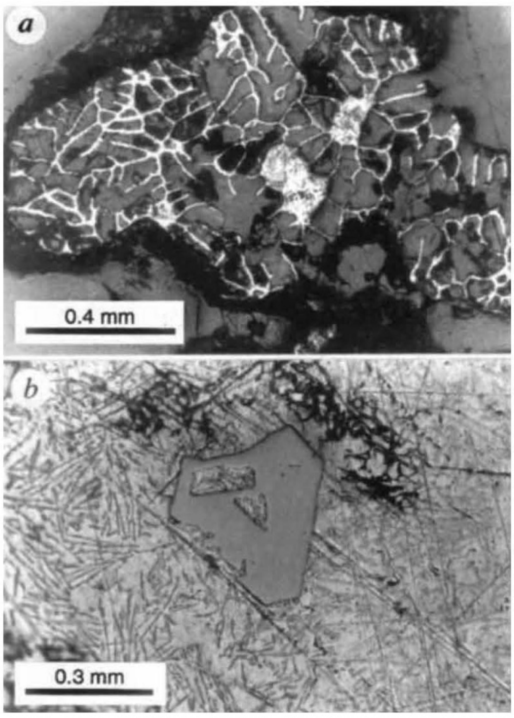
SIR — The natural occurrence of elements such as aluminium and silicon in their native form is usually ascribed to either contamination or the presence of strongly reducing fluids[1] (for example, pure methane or hydrogen, although such fluids have never been found in nature). Here we describe the formation of crystals of native aluminium, silicon, titanium, iron and platinum inside the quartz tubes that we used to sample hot volcanic gas jets associated with Kudriavy volcano on Iturup island in the Kuril arc.

The gas emitted by the volcano consists mainly of water (93–97 mol%), CO_2 (1.3–4.4 mol%), H_2S ($\leq$ 1.25 mol%) and SO_2 ($\leq$ 1 mol%), with small quantities of H_2, HCl and HF (ref. 2). It is important to note that the hydrogen concentration does not exceed 0.65 mol%, and the methane concentration is two orders of magnitude less. We determined the oxygen fugacity, f_{O_2}, by two methods: thermodynamic calculations based on the CO/CO_2 and H_2S/SO_2 of the gas, and direct measurement with an electrochemical cell[3]. All measured and calculated values lie between the Ni–NiO_2 and haematite–magnetite buffers, indicating an oxidizing environment.

Fumarole sublimates were sampled using concentric quartz tubes inserted into cleaned volcanic conduits. The upper half of each tube protrudes from the conduit and is air cooled. The two fumaroles examined by this method had gas temperatures of 930 and 705 °C — the corresponding temperature gradients in the sampling tubes were approximately 150 and 300 °C, respectively. The tubes were removed from the fumaroles after two months for laboratory examination.

In the tube from the 930 °C fumarole, we identified precipitates of aegirine, fayalite, augite, rutile, Mg-calcite, apatite, magnetite, haematite, pyrite, pyrrohtite, molybdenite, sphalerite, galena, cubanite and complex sulphides. At the hot end of the tube, thin plates of platinum and iron were found. The Pt contained a small admixture of iron ($\leq$ 0.3%) whereas the iron was pure and homogeneous.

The tube from the 705 °C fumarole was completely filled by sublimates having a total mass of 66 g and containing 78% sulphur, 12% halides (mainly NaCl and KCl) and 10% water-insoluble components. Halite and sylvite precipitated mainly in the hot part of the tube, whereas sulphur precipitates were found only in the upper part of the tube. Several minerals were identified, including SiO_2, pyrite, plagioclase, K-feldspar, clinopyroxene, aegirine, augite and radite garnet, molybdenite, avogadrite, alpazolite and complex sulphides. Associated with the minerals, we found particles of native aluminium (96.11% pure by mass) and silicon (100% pure) and one plate of titanium (99.8% pure).



Native metals from the 705 °C tube. *a*, Al-sponge with two Al droplets which diminished in size during polishing. *b*, Particle of Al+Si alloy with eutectic structure and large Si crystals.

The aluminium particles were found in the centres of Cl-rich spheres, growing outward to the rim as a sponge or honeycomb structure (*a* in the figure) and ranging in size from 0.1 to 3 mm. We could not determine the precise composition of the material in the sponge itself, but it appears to be enriched in Cl (as $AlCl_x(OH)_y$). The outermost parts of the Al are partly replaced by $KAl(SO_4)2{*}nH_2O$. The native silicon occurs both as thread- and diamond-shaped crystals within the Al, and as separate crystals (~0.1 mm in length) within Cl-rich spheres. The figure (*b*) shows one particle in which a large Si crystal is surrounded by Al–Si alloy with a texture typical of a eutectic.

Our system of sample preparation makes it unlikely that the native elements represent contamination after retrieval of the sampling tubes. The texture of the particles also argues that they formed *in situ*.

First, we note that the metals (Al, Si, Ti, Pt and Fe) formed only in zones where chlorides and fluorides precipitated and, under the sampling conditions, the halides will have remained liquid until the tubes were removed from the fumarole. We propose that the massive precipitation of halides plays a key role in the formation process of these metals. Geochemical modelling with the IVTANTERMO database[4] implies that in the volcanic gas the main Si-containing species at temperatures >700 °C would be SiO. Low-valence compounds of Al have also been described[5,6] (such as AlCl). Native Si and Al might thus have formed as a result of disproportionation reactions, for example $2SiO \rightarrow Si + SiO_2$ or $3AlCl \rightarrow 2Al + AlCl_3$ (ref. 6). The salt melt that condenses in the sampling tubes (and presumably on the inner surface of the volcanic conduits) may then trap unstable compounds such as AlCl and SiO, and provide an oxygen-free medium in which crystals of the native metals can grow. Intriguingly, particles of native aluminium have also been found associated with pure rhenium sulphide sublimates[7] at the same volcano (C. Stanley, personal communication).

To test this hypothesis, we conducted a pilot experiment in which a salt trap was placed in the jet of an 800 °C fumarole. The mixture of Si and SiO_2 that precipitated in the trap had a Si:O ratio near 1:1, suggesting a formation mechanism involving SiO. We cannot discount the possibility that conditions in the sampling tubes — in particular, disequilibrium caused by the blocking of the tube by the sublimates — also played a role. But we argue that similar precipitates of native elements could form (at least transiently) in other hydrothermal systems in which the temperature is high enough to stabilize a halide melt. The high solubility of halides in hydrothermal fluids suggests, however, that a record of this unusual process is unlikely to be preserved for a significant length in time.

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