

Discovery of Native Vanadium, a New Mineral from the Colima Volcano, State of Colima (Mexico)

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INTRODUCTION

High-temperature volcanic gases transport metals as volatile salts, oxides and in a native state (Korzinsky et al., 1996). Upon cooling, metals precipitate as minerals, which often have exotic compositions (Ostrooumov et al., 2009, and references therein). Native elements (Au, Pt, Al, and Si) in high-temperature volcanic gas precipitates have been observed at several volcanoes.

We have started to monitor the gas chemistry at Colima in January 1996, 1.5 yr after the previous 1994 eruption and almost 3 yr before the last one, which began on 20th November 1998. Colima volcano in 1996-1998 was a rare example of a flow of hot (above 800 °C) volcanic gas. High temperatures gases from Colima volcano are quite typical for a subduction type calc-alkaline andesitic volcano in terms of water content and elemental ratios.

Despite a general similarity in the condensate chemistry of Colima condensates and condensates from other volcanoes, the set of mineral precipitated from the high-temperature volcanic gas at Colima differs significantly from that obtained at other volcanoes. The mineralogy of Colima precipitates differs, in particular, by the formation of the V-enriched mineral species (Taran et al., 2000, 2001). Among them, Ostrooumov et al. (2009) described a new V-bearing mineral named colimaite (K_3VS_4).

We report here the first occurrence of native vanadium in natural fumarolic incrustations and in the mineral assemblage precipitated in silica tubes inserted into high-temperature (750-830°C) fumaroles of Colima volcano – the most active volcano of Mexico, and one of the most active in the Americas.

MINERAL NAME AND TYPE MATERIAL

Native vanadium is the second newly recognized mineral (after colimaite) that was found in both natural incrustations around high-temperature fumaroles, and in precipitated mineral assemblages in silica tubes inserted in an active fumarole within the Colima crater. Moreover, this is the second new mineral species that was discovered in Mexico after 1998 (Ostrooumov, 2011). The new mineral and its name (“vanadium”) have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (Williams et al., 2013; IMA # 2012-021a). The holotype material has been deposited in the Geological Museum of National Mexican University (New mineral collection of Mexican Mineralogical Society with cataloged under FIM 12/01).

GENERAL SETTING

Colima volcano (19°30'45"N, 103°37'W, 3855 m above sea level), the youngest and only active andesitic cone of the large Quaternary Colima volcanic complex, is located in the western portion of the Trans-Mexican Volcanic Belt, a continental arc related to the N-S convergence of the North American plate and the Cocos and Rivera plates. Historically, Colima has been the most active volcanoes in Mexico and one of the most active in the Americas with ongoing eruptions since 1998 (Taran et al., 2001 and references therein).

SAMPLING AND EXPERIMENTAL PROCEDURE

Experiments with silica tubes inserted into vents to recover samples were conducted at Colima twice in 1996. The first sample was collected by the

insertion of two 1 m long tubes into the high-temperature vent at site Z3. The first tube, Colima 1, with a diameter of 20 mm, was left for two weeks. The second one, Colima 2, with a diameter of 35 mm, remained in place for 80 days. The temperature gradient in the narrow tube was 780-350 °C, and in the wide tube, 828-380 °C. The temperature of the gas discharges at the sampling fumarolic field was in the range of 400-800 °C. Some samples were also collected in the natural incrustations of the altered rocks that are close to these silica tubes.

In the laboratory, the tubes were cut into 10 pieces corresponding approximately to 10 temperatures zones (1-2:380-420 °C; 3: 450 °C; 4: 550 °C; 5-6: 600 °C; 7: 680 °C; 8: 740 °C; 9-10: 828 °C) of each tube. The mineral precipitates that have been found in the tubes and in the natural incrustations were studied and analyzed by different analytical methods (Ostrooumov et al., 2009). Electron-microprobe, high-resolution SEM, Gandolfi technique and Glancing incidence angle X-ray diffraction (GIXD) experiments have been used to characterize the crystal chemical features of native vanadium. Quantitative elemental microanalyses were conducted with a JEOL JXA-8900R electron microprobe by wavelength-dispersion spectroscopy (WDS) operated at 20 kV, 20 nA, in a focused beam mode.

OCCURRENCE, APPEARANCE AND PHYSICAL PROPERTIES

Firstly, the native vanadium crystals precipitated in a narrow temperature interval 550-680 °C (zones 4-7: see above). They were found in both silica tubes (Colima 1 and Colima 2) in the same temperature interval with two associated mineral phases: colimaite, K_3VS_4 , and shcherbinaite, V_2O_5 . These V

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compounds were associated with other minerals in the silica tube experiment: sulfates, oxides, chlorides, fluorides and native gold. Twenty-one phases have been identified in the Colima silica tubes. The main non-silicate phases are not halite and sylvite as at other volcanoes, but pure and mixed Na- and K-sulfates enriched in V, Cu and Zn. These sulfates are enriched in V between 400 and 600 °C up to pure VO (SO₄) (Ostrooumov & Taran, 2001; Taran et al., 2001).

The particles of vanadium are found in silica tubes on a very thin layer on a glassy-like thicker support. Vanadium forms smooth, irregular to flattened crystals 5-20 µm in diameter. Smaller irregular crystals have also been observed in silica tubes.

Native vanadium has subsequently been found in the rock adjacent to the fumarole in the natural wall matrix (Fig. 1A-B). Native vanadium was found in these natural incrustations, where it is also associated with colimaite, K₃VS₄' and shcherbinaite, V₂O₅. The vanadium crystals in these mineralogical assemblages are close by morphology (irregular to flattened) to those crystals in silica tubes. At the same time, some vanadium crystals in the altered rocks reach larger sizes than the observed in the silica tubes.

ANALYTICAL RESULTS

Chemical Composition

The preliminary qualitative energy-dispersive analyses (EDS) in the zone of the particles with V-dominant alloy, showed that of the elements with Z > 4, only V, Fe, Al, and Ti were present with the predominance of first element (Fig. 1C). An EDS spectrum indicated the presence of these elements and was identical to that of native vanadium crystals recovered on the silica tubes and in the adjacent rocks. Many EDS spectra were obtained and the EDS chemical mapping was performed not only on the vanadium particles but also on their environs. These maps also indicate the existence of V, Fe, Al, and Ti in the vanadium particles. Important to note is that the presence of Ca and S corresponds to the calcium sulfates from the silica tube matrix.

The obtained data give relevant information on the composition of vanadium particles although the

element percentage presents some variations in these sites. Results of four electron-microprobe analyses were averaged to yield an empirical formula of vanadium. Four analyses of vanadium crystals by EPMA yield (wt%) V 87.03.29, Fe 10.24, Al 2.21, Ti 0.49, with total sum 99.97 (wt%). No other elements with atomic number > 4 were detected. The empirical formula is V_{0.86}Fe_{0.09}Al_{0.04}Ti_{0.01}. The simplified formula is V.

X-ray Crystallography

Single-crystal X-ray studies could not be carried out due to the size of the vanadium crystals. Vanadium was first recognized as a new mineral by its Gandolfi pattern, which does not match any natural phase in the JCPDF fil. X-ray powder-diffraction data are calculated by analogy with those of pure vanadium. Unit cell parameters refined from the powder data are as follows: space group Im3m, with a=3.022 (3), V=27.60 (5) Å³, and Z=2. The five strongest calculated diffraction lines from this natural compound are [d spacings in Å, (l) (hkl)]: 2.1411 (100) (200), 1.5141 (12) (200), 1.2363 (19) (211), 0.9575 (8) (310), and 8.8091 (11) (321).

After glancing incidence angle X-ray diffraction experiments, an automatic peak search procedure (JADE 9.0 software of RIGAKU Ltd.) combined with the diffraction data from several structural and mineralogical digital databases have allowed also the identification of three V-enriched phases: native vanadium, colimaite and shcherbinaite. Thus, this diffraction method has confirmed the results that have been obtained by the Gandolfi-type X-ray diffraction.

CONCLUSIONS

Native vanadium has not been reported before our discovery in the mineralogical assemblages of the studied volcanic fumarolic zone. This paper reports the first finding of native vanadium in mineral precipitates from high-temperature (~800 °C) volcanic vapors of the Colima volcano, Mexico. Smooth, irregular and flattened of native vanadium crystals 10-20 µm in dimension were found on the inner wall of a silica tube inserted into an 800 °C fumarolic vent and in the natural incrustations of Colima volcano. Vanadium precipitates cover a narrow temperature range of 550-680 °C, and

occur in association with colimaite and shcherbinaite. The set of mineral precipitated from the high-temperature volcanic gas at Colima differs significantly from that obtained at other volcanoes. In contrast to other volcanoes with reduced volcanic gas very oxidized Colima gases do not precipitate halite, sylvite, molybdenite or greenockite, but precipitate V-minerals (colimaite, shcherbinaite and pauflerite), V-enriched phases (Na-K sulfates), and some native elements (vanadium and gold).

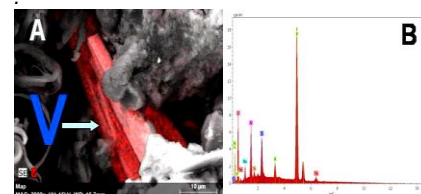


fig 1. A) Crystals of vanadium collected in the natural incrustations that are observed using a JEOL JXA-8900R SEM (BSE image); B) EDS spectrum from a vanadium-particle.

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