

BISMUTH TELLURIDES AND SULFIDE MIXTURES AND THEIR RELATION TO METAL FROST ON VENUS. S. T. Port¹, E. Kohler², and V. Chevrier¹, ¹University of Arkansas, Fayetteville, AR, 72701; ²NASA Goddard. (saraport@email.uark.edu)

Introduction: In the 1960s radar analysis of the surface of Venus uncovered high radar reflectivity regions on the highlands and mountain ranges [1-2]. Depending on the mountain range these reflective regions generally manifest between 2.5 and 4.75 km above the planetary radius of 6051.0 km [3-6]. Above this critical altitude the reflectivity rapidly decreases until it matches the same reflectivity as the lowlands [3].

The source of this anomaly is still a puzzle among researcher, however it has been postulated that its appearance is due to surface roughness, precipitation from the atmosphere, or an unknown interaction between the surface and the atmosphere [2, 7]. Most researchers believe that one of the two latter scenarios is the most likely culprit [7, 8-11]. This reflective coating has since been named “metal frost” [7].

Potential candidates suggested in the literature for the metal frost include tellurium (Te), bismuthinite (Bi₂S₃), or a lead bismuth sulfosalt [3-5, 7, 10]. Tellurobismuthite (Bi₂Te₃) has also been considered because it has a high dielectric constant which would produce the high reflectivity signal seen in the mountain ranges [9]. However preliminary experimentation completed by Kohler *et al.* on Bi₂Te₃ and Bi₂S₃ showed stability at lowland and highland Venus temperatures, thus weakening the argument that it is the source of the metal frost [9]. Tellurium was also tested and it was found that tellurium readily oxidizes in a CO₂ environment [9]. We propose that some mixture created through a blend of bismuth, tellurium, and sulfur might provide the solution to the metal frost dilemma.

Methods: Three blends of bismuth, tellurium, and sulfur were chosen for the experiments. These mixtures were a 1:1 molar ratio of Bi₂S₃ and Bi₂Te₃, a 1:3 molar ratio of Bi₂S₃ and Te, and a 1:1:1 molar ratio of Bi, Te, and S, respectively. Each mixture was tested at three different temperatures representing the temperature gradient from: the Venusian lowlands, the critical altitude, and to the highest point on Venus (the top of Maxwell Montes). These three temperatures were 460°C (0 km), 425°C (4.5 km), and 380°C (11 km), respectively. Each mixture was first weighed and inserted into a Lindberg tube oven for 24 hours filled with one of three atmospheric compositions: pure CO₂, 100 ppm of SO₂ in CO₂, or 100 ppm of COS in CO₂. Additionally the 1:1 molar ratio of Bi₂S₃/Bi₂Te₃ mixture was placed into the Venus Simulation Chamber at the University of Arkansas at three simulated conditions on Venus: 460°C/95 bar, 425°C/75 bar, and 380°C/45

bar. These experiments were completed in pure CO₂ for 24 hours.

After the completion of each experiment, each sample was weighed once more and analyzed via X-Ray Diffraction (XRD) in order to determine any compositional changes that occurred to the samples during the experiments.

Results: XRD analysis revealed that the Bi₂S₃/Bi₂Te₃ experiments completed in the chamber and the oven in pure CO₂ have near identical results. For all experiments at all temperatures and pressures the most common minerals found were Bi₂Te₂S, Bi₂Te₃, Bi₂S₃, and BiTe. In both oven and chamber experiments Bi₂S₃ quickly becomes less abundant when it was heated, with nearly little or no Bi₂S₃ by 460°C. One noticeable difference between the chamber and the oven experiments was the formation of elemental sulfur in the chamber and the formation of Bi₂O₃ in the 460°C experiment (Table 1a and 1b).

In the Bi₂S₃/Bi₂Te₃ CO₂/SO₂ oven experiments both Bi₂O₃ and TeO₂ formed. Meanwhile Bi₂Te₃ was present in both temperatures while Bi₂S₃ was not. Unexpectedly in both the Bi₂S₃/Te and Bi/Te/S CO₂/SO₂ experiments at all temperatures Bi₂Te₂S formed, but no oxides. In the Bi₂S₃/Te experiments Bi₂Te₃ was present in both temperatures while Bi₂S₃ was only found in the 460°C experiment. Lastly in the Bi/Te/S CO₂/SO₂ experiment Bi₂Te₂S was the only mineral that was formed as well as some elemental bismuth and tellurium (Table 1c).

The Bi₂S₃/Bi₂Te₃ and Bi₂S₃/Te CO₂/COS oven experiments produced a plethora of minerals and elements. However, in the Bi/Te/S experiment at 380°C only two minerals were formed, Bi₂Te₂S and Bi₂Te₃ (Table 1c).

Table 1: a) The results of the Bi₂S₃/Bi₂Te₃ experiments completed in the chamber in pure CO₂ b) Bi₂S₃/Bi₂Te₃ experiments in the oven in pure CO₂ c) The results of experiments completed in 100 ppm of SO₂ in CO₂ and the results of experiments completed in 100 ppm of COS in CO₂. Results are listed in order of how well the spectra matched the XRD database. *only appeared in one experiment.

a)

460°C/95 bar	425°C/75 bar	380°C/45 bar
Bi ₂ Te ₂ S	Bi ₂ Te ₂ S	Bi ₂ Te ₂ S
BiTe	Bi ₂ S ₃	Bi ₂ S ₃
Bi ₂ O ₃	Bi ₂ Te ₃	Bi ₂ Te ₃
S	BiTe*	Bi*
		S*

b)

	460°C	425°C	380°C
Bi ₂ S ₃ /Bi ₂ Te ₃	Bi ₂ Te ₂ S	Bi ₂ Te ₂ S	Bi ₂ Te ₂ S

	Bi ₂ Te ₃ Bi ₂ S ₃ BiTe	Bi ₂ Te ₃ Bi ₂ S ₃ BiTe	Bi ₂ Te ₃ Bi ₂ S ₃ BiTe
Bi₂S₃/Te	Bi ₂ Te ₂ S Bi ₂ Te ₃	Bi ₂ Te ₂ S Bi ₂ S ₃ Te*	Bi ₂ Te ₂ S Bi ₂ S ₃ Te*
Bi/Te/S	Bi ₂ Te ₂ S BiTe	Bi ₂ Te ₂ S BiTe	Bi ₂ Te ₂ S Te Bi ₂ S ₃

c)

	CO ₂ /SO ₂		CO ₂ /COS	
	460°C	380°C	460°C	380°C
Bi₂S₃/Bi₂Te₃	Bi ₂ Te ₃ Bi ₂ O ₃ TeO ₂	Bi ₂ Te ₃ Bi ₂ O ₃ BiTe TeO ₂	Bi ₂ Te ₃ Bi ₂ Te ₂ S BiTe Bi ₂ S ₃ * Bi ₂ O ₃ * S*	Bi ₂ Te ₂ S Bi ₂ S ₃ Bi ₂ Te ₃ Bi ₂ O ₃ BiTe
Bi₂S₃/Te	Bi ₂ Te ₂ S Te Bi ₂ S ₃ Bi ₂ Te ₃	Te Bi ₂ Te ₂ S Bi ₂ Te ₃	Bi ₂ Te ₃ Te Bi ₂ O ₃ Bi	Bi ₂ Te ₂ S Te Bi ₂ S ₃ Bi ₂ Te ₃ Bi ₂ O ₃ BiTe
Bi/Te/S	Bi ₂ Te ₂ S* Te* Bi*	Bi ₂ Te ₂ S* Te* Bi*	- - -	Bi ₂ Te ₃ * Bi ₂ Te ₂ S*

Discussion: The results from the chamber and the oven were near identical except for the formation of elemental sulfur in the chamber. The cause is because the oven is not perfectly sealed, and at these temperatures sulfur vaporizes and subsequently leaves the system. In the sealed chamber sulfur vaporizes, only to deposit onto the sample at the end of the experiment when the temperature cools down to the ambient temperature. The vaporization of sulfur also explains the diminishing amount of Bi₂S₃ in every experiment, both oven and chamber.

In all experiments with the Bi₂S₃/Te mixture Bi₂Te₃ and Bi₂Te₂S were both created demonstrating some replacement of S with Te. However, the corresponding amount of sulfur is absent which is most likely due to the vaporization of sulfur.

One unexpected result was the formation of Bi₂Te₂S in nearly all of the experiments except for the Bi₂S₃/Bi₂Te₃ CO₂/SO₂ experiments. Our hypothesis is that in the Bi₂S₃/Te and the Bi/Te/S experiments tellurium is unbonded, however tellurium is highly reactive and so will bond very quickly. The increased temperature results in the vaporizing of sulfur which leads to more unbonded bismuth. The tellurium will then quickly form Bi₂Te₂S and Bi₂Te₃. However, in the Bi₂S₃/Bi₂Te₃ experiment tellurium is already bound to bismuth making it stable. As Bi₂S₃ breaks apart and the sulfur vaporizes bismuth begins to bind to oxygen from the dissociated SO₂ creating Bi₂O₃. Any tellurium that breaks apart from Bi₂Te₃ then has no alternative but to bond to oxygen producing TeO₂. This is not seen

in the CO₂ experiments because SO₂ is less stable than CO₂ and therefore more likely to react to the solid mixtures. For the CO₂/COS experiment, COS has half the amount of oxygen than SO₂ so once Bi₂O₃ is formed there is little oxygen left for tellurium to form TeO₂.

All Bi/Te/S mixture experiments resulted in the least amount of mineral formations, generally one or two. This demonstrates that without any preexisting bonds between elements the subsequent minerals that are formed are simple and straightforward.

All experiments completed in CO₂/COS, except for the Bi/Te/S experiments resulted in an array of minerals and elements, thus demonstrating that interactions between COS and the bismuth, tellurium, and sulfur mixtures are complicated and are not well understood. Analysis of the gas composition after the experiment via a gas chromatograph may help elucidate the chemical reactions that occur during the experiment.

Conclusion: All minerals formed at the end of the experiments showed some stability at all tested temperature conditions. However, not all mixtures were tested at Venusian pressures. It is possible that our results will vary if all of the experiments are completed at Venus pressures using the chamber. At this point the source of metal frost cannot be determined, however a clear candidate may emerge when the samples are tested in the chamber with the mixed gases.

Future Work: All experiments completed in the mixed gases (CO₂/COS and CO₂/SO₂) in the oven will be completed in the Venus simulation chamber to observe the effects of pressure. All bismuth, tellurium, and sulfur mixtures that were not tested at 425°C will be completed. The chamber will be attached to a gas chromatograph which will be used to analyze the atmospheric composition after each experiment.

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