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NOMENCLATURE OF PLATINUM-GROUP-ELEMENT ALLOYS: REVIEW AND REVISION[1]

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ABSTRACT

The nomenclature of Os–Ir–Ru alloys, as revised by its Nomenclature Subcommittee, has been approved by the Commission of New Minerals and Mineral Names, International Mineralogical Association. Henceforth, only four names apply to minerals whose compositions (in at.%) lie within the ternary system Os–Ir–Ru: osmium for all hexagonal alloys with Os the major element; iridium for all cubic alloys with iridium the major element; rutheniridosmine for all hexagonal alloys with Ir the major element; and ruthenium for all hexagonal alloys with Ru the major element. The nomenclature of alloys of platinum-group elements in the ternary systems Os–Ir–Pt, Ru–Ir–Pt, Ir–Ru–Rh, Ir–Os–Rh and Pd–Ir–Pt are reviewed.

Keywords: nomenclature, Os–Ir–Ru alloys, osmium, iridium, ruthenium, rutheniridosmine, iridosmine, osmiridium, platiniridium, platinum-group-element alloys, ternary systems.

SOMMAIRE

La nomenclature des alliages de Os–Ir–Ru, tel que révisé par un sous-comité chargé de cette question, a reçu l'approbation de la commission des nouvelles espèces minérales et des noms de minéraux de l'Association Internationale de Minéralogie. Dorénavant, quatre noms seulement seront utilisés pour décrire les minéraux dont les compositions (en pourcentages atomiques) correspondent à ce système ternaire: *osmium* pour tout alliage hexagonal dans lequel Os est l'élément majeur; *iridium* pour tout alliage cubique ayant Ir comme élément majeur; *rutheniridosmine* pour tout alliage hexagonal ayant Ir comme élément majeur, et *ruthénium* pour tout alliage hexagonal ayant Ru comme élément majeur. Nous examinons aussi la nomenclature des alliages des éléments du groupe du platine des systèmes ternaires Os–Ir–Pt, Ru–Ir–Pt, Ir–Ru–Rh, Ir–Os–Rh et Pd–Ir–Pt.

(Traduit par la Rédaction)

Mots-clés: nomenclature, alliages Os–Ir–Ru, osmium, iridium, ruthénium, rutheniridosmine, iridosmine, osmiridium, platiniridium, alliages des éléments du groupe du platine, systèmes ternaires.

INTRODUCTION

Harris & Cabri (1973) proposed a new nomenclature for minerals whose compositions lie in the ternary system Os–Ir–Ru. That proposal was based on a study of Os–Ir–Ru minerals from several countries, high-temperature phase-equilibrium data on the three binary systems, a review of previous systems of nomenclature (*e.g.*, Hey 1963), and was approved in 1972 by a vote of the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA). Several comments were made by CNMMN members, and were discussed by Harris & Cabri (1973); in particular, a suggestion was made to add boundary lines parallel to the Ru–Os and Ru–Ir edges, which was implemented. The success and acceptance of this nomenclature by those who work with Os–Ir–Ru alloys were immediate and worldwide. Indeed, there has not been a single criticism of this nomenclature in any publication reporting compositions of platinum-group-element (PGE) alloys.

Since "iridosmine" and "osmiridium", as redefined by Hey (1963), were also in common usage for binary Os–Ir alloys, Harris & Cabri (1973) included these names in their proposed nomenclature, knowing full well that, *sensu stricto*, the names should not be maintained for ternary compositions. In a similar manner, the name "platiniridium" was "...... retained for historical reasons only ....." (Cabri & Hey 1974).

In 1983, the CNMMN began receiving a number of proposals for other alloys of the platinum-group elements, named on a similar basis. Voting on these proposals was suspended by the CNMMN pending an investigation into the practicality of extending the Harris & Cabri nomenclature to other alloy systems. Also, the publication of general guidelines on nomenclature by Nickel & Mandarino (1987), under the auspices of the CNMMN, made some aspects of the 1973 nomenclature questionable, in particular, the application of adjectival modifiers. In 1988, the Nomenclature Subcommittee put together a proposal

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entitled "Solid Solutions in Mineral Nomenclature" (SSMN) to be used as an internal document to assist the CNMMN in maintaining a consistent approach to the nomenclature of mineral phases that occur in solid-solution series. One of the rules of this document states that for a complete solid-solution

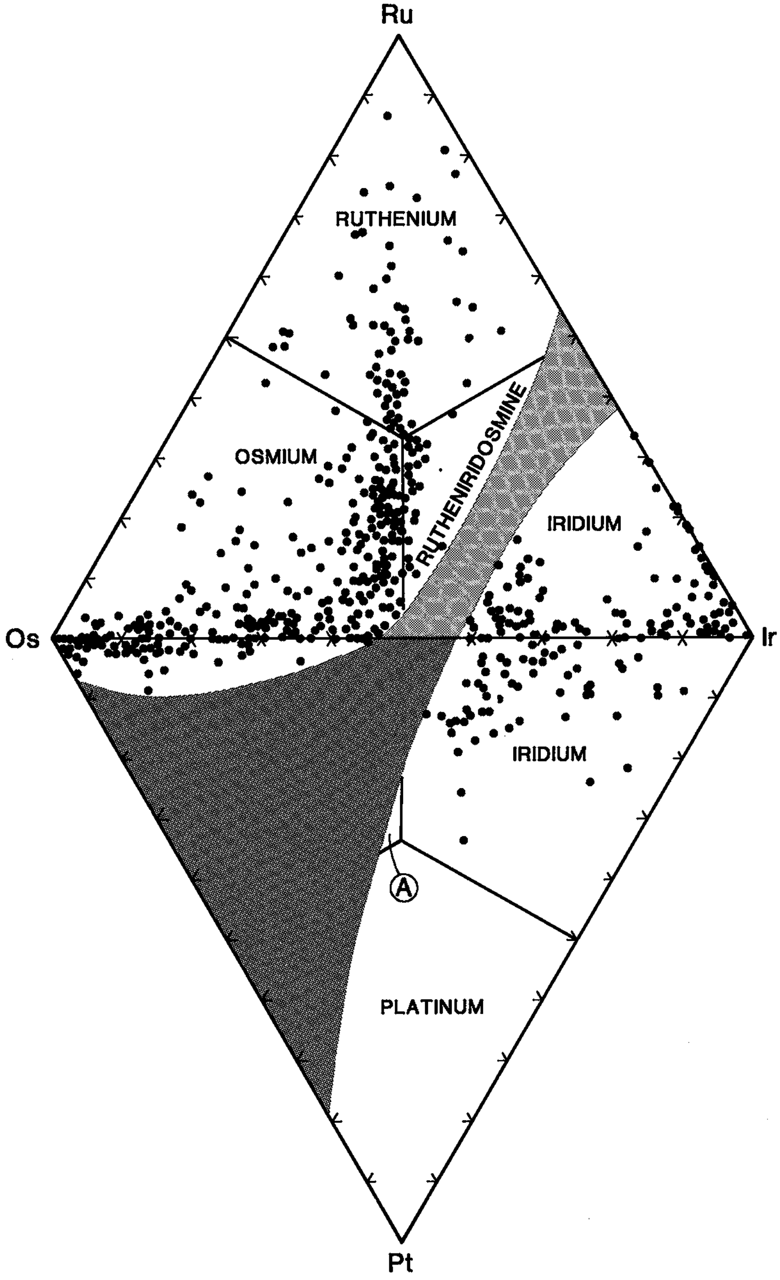

FIG. 1. The ternary systems Os–Ir–Ru and Ir–Os–Pt showing the CNMMN-approved nomenclature. The miscibility gaps in both ternary systems are based on a combination of analyses of PGE alloys and experimental data available. Another version of the miscibility field for the Ir–Os–Pt system is shown in Figure 2. Data points as recorded in text. Area A is discussed in the text.

series without structural ordering of the ions, the end members are divided at 50 mole %, and the two portions are given different names (50% rule). When the 50% rule is applied to members of ternary solid-solution series, the mineral names should be given only to the end members. Each name should apply to the compositional range from the end member to the nearest right bisectors of the sides of the compositional triangle. In addition, the CNMMN voted that these rules be applied to current and future proposals concerning the PGE alloys and that the Harris & Cabri nomenclature for the Os–Ir–Ru system be changed to conform with these same rules.

The purpose of this paper is to document the revision of the nomenclature of alloys in the Os–Ir–Ru system and to review the nomenclature of ternary systems consisting solely of PGE alloys.

DISCUSSION

To conform with the 50% rule, the compositions that plot in the Os–Ir–Ru system should be renamed as shown in Figure 1. This Figure is a compilation of all compositions determined, known to us at this date; the large data-base clearly defines for natural occurrences a miscibility gap that extends from 53 to 42 at.% Os on the Os–Ir binary join. This compares to the high-temperature values of 62.7 and 41.7 at.% Os, determined by Reiswig & Dickinson (1964). As suggested by Bird & Bassett (1980), the difference between the Os boundary of the miscibility gap (62.7 at.% Os) obtained from experimental data (2660°C, 1 bar) and the 53 at.% Os obtained for natural occurrences may be due to the effect of crystallization at high pressures. For the Ru–Ir binary, the high-temperature data of Eremenko *et al.* (1988), which show a miscibility gap from 54 to 38 at.% Ru, fit the data from natural alloys quite well. The data for the plotted natural alloys are derived from the following articles, as well as unpublished data: Augé (1985), Begizov *et al.* (1975), Bird & Bassett (1980), Bowles (1981), Cabri *et al.* (1981), Cabri & Genkin (1991), Cabri & Harris (1975), Cabri & Hey (1974), Cabri & Laflamme (1988), Cowden *et al.* (1990), Distler *et al.* (1989), Feather (1976), Ford (1981), Hagen *et al.* (1990), Harris & Cabri (1973), Jen & Teng (1973), Johan *et al.* (1990), Lévy & Picot (1961), Mao & Zhou (1989), Rudashevsky & Zhdanov (1983), Shilo *et al.* (1980), Slansky *et al.* (1991), Snetsinger (1971), Stockman & Hlava (1984), Stumpfl & Clark (1966), Stumpfl & Tarkian (1973), Tarkian (1987), Toma & Murphy (1977), Urashima *et al.* (1974) and T. Weiser (priv. comm.).

In order to plot the analytical data in the respective triangular diagram, the weight percentages of the elements were calculated such that the total is one atom and then the three major elements were recalculated as mole percent end-members, ignoring the remaining elements. No attempt was made to combine elements, because there are no clear rules for which elements should be combined, even though this has been done in the literature, in an *ad hoc* manner. Our approach has some drawbacks in cases where the third and fourth most abundant elements have similar atomic percentages; thus, the accuracy

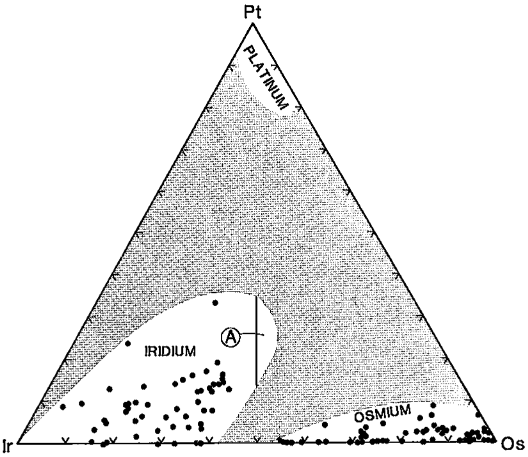

FIG. 2. The ternary system Ir–Os–Pt shown in Figure 1 redrawn with a very broad miscibility gap, postulated to extend from the Pt–Ir binary on the basis of data of Raub & Plate (1956). Area A is discussed in the text.

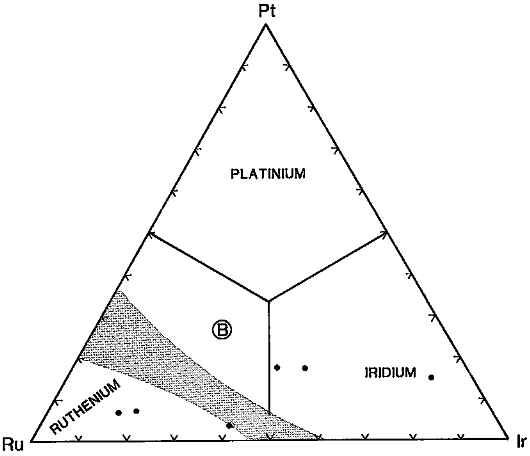

FIG. 3. The ternary system Ru–Ir–Pt, with miscibility gap based on our data in Figure 1 for the Ru–Ir binary, those of Eremenko *et al.* (1988) for the Ru–Ir binary, and Hutchinson (1972) for the Ru–Pt binary. Data points in the iridium field are from Hagen *et al.* (1990), Tarkian (1987) and the "platiniridium" of Cabri & Hey (1974). Data points in the ruthenium field are from Hagen *et al.* (1990), Tarkian (1987) and T. Weiser (priv. comm.). Area B is discussed in the text.

of analysis for such data is critical. Feather (1976) reported a large number of compositions of alloys in the ternary system Os–Ir–Ru for which Os was determined by difference, owing to the use of an unsuitable Os standard. Feather concluded that the few compositions that plot within the miscibility gap had been underestimated for Os; these results, therefore, were rejected by us. We have also chosen not to include from the literature those compositions whose analytical totals are in the range 90 - 95 wt.% and those done by energy dispersion, because the results are considered to be unreliable.

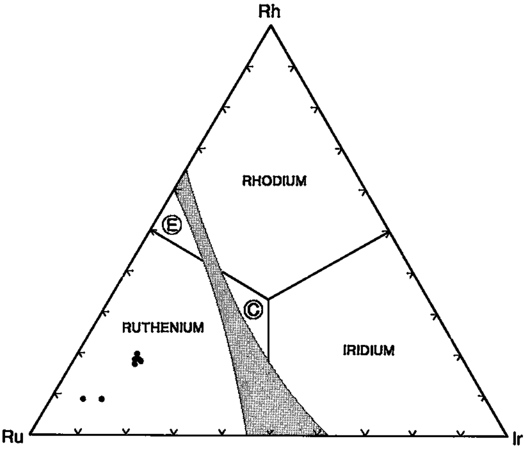

FIG. 4. The ternary system Ru–Ir–Rh, with the miscibility gap based on the data of Eremenko *et al.* (1988) for the Ru–Ir binary, and of Paschoal *et al.* (1984) for the Ru–Rh binary. Data points in the ruthenium field include the ruthenium of Urashima *et al.* (1974) and the "iridrhodruthenium" of Mao & Zhou (1989). Areas C and E are discussed in the text.

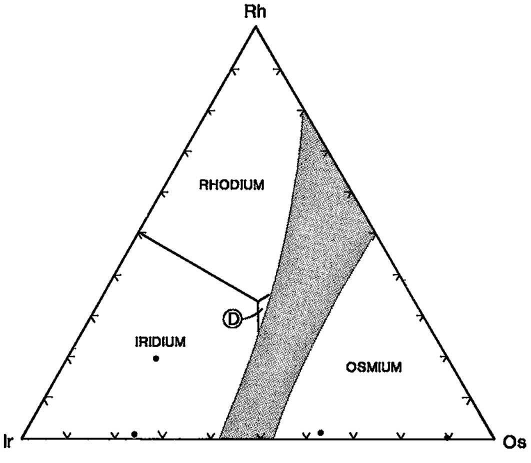

FIG. 5. The ternary system Ir–Os–Rh, with the miscibility gap in the Ir–Os binary from our data in Figure 1 and from the Rh–Os binary of Korenovskii *et al.* (1985). The data points are from Stumpfl & Tarkian (1973) and T. Weiser (priv. comm.). Area D is discussed in the text.

Experimentally derived limits for the miscibility gap only apply to very high temperatures and for systems free of impurities, but remain a useful guide to compositional ranges that may be expected in natural occurrences. It follows that there will be other related PGE-alloy systems that should follow similar rules of nomenclature. It must be understood, however, that the experimental data-base is very limited. Data are available for all PGE binary joins, but are usually limited to high temperatures (*e.g.*, 1500 or 1700°C). Thus, several miscibility gaps are reported to occur at high temperatures, or are predicted to occur at low temperatures, in several PGE binary systems. These gaps are proposed even where both end-members have similar unit cells and space groups (*e.g.*, Pt and Ir). A further difficulty in resorting to the high-temperature experimental data for *binary* systems is that experimental data in *ternary* systems are available only for Ru–Rh–Pd at 1700°C (Paschoal *et al.* 1983). Therefore, the location of the miscibility gaps in ternary PGE systems should be guided by mineral assemblages.

Natural alloys also have been reported to occur in the following ternary systems: Os–Ir–Pt, Ru–Ir–Pt, Ir–Ru–Rh, Ir–Os–Rh, and Pd–Ir–Pt. The Os–Ir–Pt system has a large miscibility gap, and is shown with the Os–Ir–Ru system in Figure 1. The exact extent and shape of the miscibility gap in the Os–Ir–Pt system, using the gap on the Os–Ir binary as a starting point, are somewhat speculative, as no experimental data are available. The miscibility gap on the Pt–Os binary join is drawn using the $Pt_{80}Os_{20}$ limit at 1500°C (Voronova *et al.* 1984) and the compositions of natural alloys. The experimentally derived limit (at 1500°C) of $Os_{95}Pt_5$ for the Pt–Os binary obviously does not apply to the compositions of natural alloys.

Pt and Ir have very similar unit-cell edges (3.9231 and 3.8394 Å, respectively), the same space group (*Fm*3*m*), and form a complete solid-solution at high temperatures. However, a miscibility gap occurs on cooling (Raub & Plate 1956). The gap extends from 7 to 99 at.% Ir at 700°C, making it unlikely that pure (Ir,Pt) exists in nature. Thus, the platiniridium of Cabri & Hey (1974) cannot be plotted in this ternary system and may, in fact, be a ternary Ir–Ru–Pt or even a Ir–Ru–Pt–Os alloy. It should be noted that area A, which could be larger (as shown in Fig. 2) or smaller, represents the compositional range for a potential new mineral species, *i.e.*, a cubic Os-dominant alloy.

Natural alloys in the system Ru–Ir–Pt are shown in Figure 3. The miscibility gap on the Pt–Ru binary was determined at 1000°C by Hutchinson (1972); the gap on the Ir–Ru binary is from Eremenko *et al.* (1988). Thus, the triangular diagram as shown here has an area (B) in which a cubic Ru-rich phase is present; if a cubic alloy with that composition is found, it would qualify for a new mineral name. However, phase relations at low temperatures are complicated by the very broad miscibility gap on the Pt–Ir binary join (Raub & Plate 1956), which was discussed above, but this complication is not included in Figure 3.

Figure 4 shows the compositions of natural alloys occurring in the system Ru–Ir–Rh. The narrow miscibility gap on the Rh–Ru binary is taken from the experimental data of Paschoal *et al.* (1984), and that on the Ru–Ir binary is from Eremenko *et al.* (1988). Should a cubic Ru-dominant mineral be found that plots in area C, it would qualify as a new mineral species. Likewise, a hexagonal Rh-dominant mineral with a composition in area E also would qualify as a new species. Once again, serious complications at low temperatures could be present on the Rh–Ir binary; Moffatt (1984) stated that a broad miscibility gap (between Rh_{90} and Ir_{90}), though not observed experimentally, is highly probable, based on the data of Raub (1959).

Natural alloys also occur in the system Ir–Os–Rh (Fig. 5). The miscibility gap on the Rh–Os binary is derived from the 1500°C experimental data of Korenovskii *et al.* (1985), and on the Ir–Os binary from our data in Figure 1. As with the system Ru–Ir–Rh, phase relations would be greatly complicated should the prediction (Moffatt 1984) of a broad miscibility gap at low temperatures on the Rh–Ir binary prove to be correct. Such a gap would make it unlikely that an alloy plotting in area D would be found. On the other hand, no experimental data are available for the ternary system.

Finally, Cabri & Laflamme (1974) reported an alloy in the system Ir–Pd–Pt (Fig. 6) as platinum. In this ternary system, all three binaries show complete miscibility at high temperature. In addition, the Pt–Ir (Raub & Plate 1956) and the Ir–Pd (Raub & Plate 1957) binary systems show very broad miscibility gaps, and a similar gap also is considered highly probable for the Pt–Pd binary (Raub 1959). Therefore, the boundaries delimiting the extent of Pt solid solution in the ternary system (Fig. 6) are based on a combination of the medium-temperature experimental data cited and the single datum of Cabri & Laflamme (1974). The broad miscibility area as drawn, however, must remain speculative because, once again, there are no experimental data available on the ternary system.

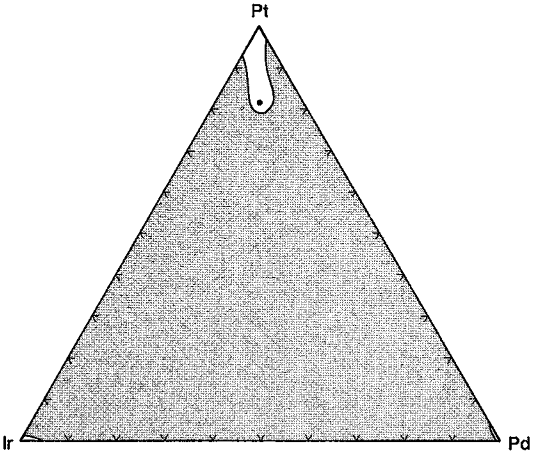

FIG. 6. The ternary system Ir–Pd–Pt, with the very large miscibility gap based on a single data-point from Cabri & Laflamme (1974) and on the experimental data of Raub & Plate (1956, 1957) and Raub (1959).

CONCLUSIONS

Based on the new rules of nomenclature, as recommended by the Nomenclature Subcommittee and approved by the CNMMN–IMA, the PGE alloys, particularly those in the system Os–Ir–Ru, are to be revised as follows:

1) the mineral names "iridosmine", "osmiridium", and "rutheniridosmium" are no longer valid and should no longer be used. Therefore, alloys with compositions in the field of "iridosmine" are now osmium. Likewise, alloys called "osmiridium" and "ruthenosmiridium" are now iridium.

2) the mineral name rutheniridosmine is retained, but its compositional field is restricted to hexagonal Os–Ir–Ru alloys in which Ir is the dominant element.

Following this newly revised nomenclature, we have reviewed the literature and therefore propose that:

1) "platiniridium" no longer be used; minerals formerly so named are to be known as platinian iridium.

2) for the ternary system Os–Ir–Pt, there is potential for a total of four minerals, of which osmium, iridium, and platinum are known. The compositional field for a cubic Os-dominant alloy denotes a potential new mineral.

3) for the ternary system Ru–Ir–Pt, there is potential for four minerals, of which ruthenium, iridium, and platinum are known. The compositional field for a cubic Ru-dominant alloy denotes a potential new mineral.

4) for the ternary system Ru–Ir–Rh, there is potential for five minerals, of which ruthenium, iridium, and rhodium are known. The compositional fields for a cubic Ru-dominant alloy and a hexagonal Rh-dominant alloy denote two potential new minerals.

5) for the ternary system Ir–Os–Rh, though there is potential for four minerals, it is unlikely that an alloy will be found with a composition in the remaining unnamed field. The known minerals are iridium, osmium, and rhodium.

6) for the ternary system Ir–Pd–Pt, the three minerals are iridium, palladium, and platinum.

Finally, we note that there is no universally accepted method of plotting compositions in the ternary systems we have discussed. Until such an agreement is reached, we suggest that authors clearly define their methodology.

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